

# COMMERCIAL ORGANIC ANALYSIS

A TREATISE ON

THE PROPERTIES, MODES OF ASSAYING, AND PROXIMATE  
ANALYTICAL EXAMINATION OF THE VARIOUS  
ORGANIC CHEMICALS AND PRODUCTS  
EMPLOYED IN THE ARTS, MANU-  
FACTURES, MEDICINE, Etc.

WITH CONCISE METHODS FOR

THE DETECTION AND DETERMINATION OF THEIR IMPURITIES  
ADULTERATIONS, AND PRODUCTS OF DECOMPOSITION

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VOLUME II—PART I

FIXED OILS, FATS, WAXES, GLYCEROL, NITROGLYCERIN  
AND NITROGLYCERIN EXPLOSIVES

WITH REVISIONS AND ADDENDA BY THE AUTHOR AND

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## REVISER'S NOTE TO THIRD EDITION.

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Although the time available for the preparation of the present volume was brief in proportion to the task, it was so much greater than that allotted to Volume I that, as will be noted, a much more extensive revision has been accomplished. It has still been impracticable to submit manuscript or proof-sheets to Mr. Allen, but an extended correspondence has secured his co-operation in many respects, and he has forwarded a large amount of manuscript notes, clippings, and references which have been utilised.

It will be noted that the plan of distinguishing the added matter by the use of a smaller type, which was employed in Volume I, has been followed but rarely in this volume. This is because the revision has been such as to involve every page and nearly every paragraph, to indicate the new matter would bring about such a mixture of different types as would confuse the work. It must, therefore, be understood that the American reviser is responsible for all omissions and for all errors in fact or form. In justice to Mr. Allen, it must be remembered that his control of the work has been at long range, and he has been unable to add to it the innumerable hints and items of advice which his large practical experience and wide familiarity with the literature of the subjects would have suggested if the book had been preparing under his direct supervision. It is believed, however, that the work does not misrepresent him in any important particular. In deference to his publicly expressed disapproval of the spelling advised by the American Association for the Advancement of Science, it has not been adopted, and any instances are accidental.

The preparation of the revision would have been much delayed if the reviser had not been aided by his friend and colleague, Dr. William Beam, who has devoted the greater portion of several months to the selection and arrangement of the data. The results of Dr. Beam's faithful and intelligent labors are seen in every part of the work.

It is not wise, perhaps, to make an excuse in a preface, but it seems not improper to call attention again to the fact that the hasty revision

of these volumes has been rendered necessary by the danger of the unauthorised reprinting of them—an act which would misrepresent the author and infringe upon his rights.

By Mr Allen's advice, the matter originally in Volume II has been distributed into two parts. Part Second, which is now in process of revision, will include the hydrocarbons and immediate derivatives. The chapter on the terpenes and closely related bodies will be largely revised by Mr Allen, and will necessarily be extensive, since great progress has been made of recent years in this department of organic chemistry.

Among the important additions to the present volume are —The bromine thermal method, methods for determination of glycerol, acetyl number, various tests for oxidation of oils, composition and official methods for examination of dynamites and smokeless powders, dégras, and cloth oils. The tables on pages 91 to 102 were furnished by Mr Allen.



## PREFACE TO SECOND EDITION.

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I feel that I cannot allow this volume to appear without a few words of apology, explanation, and thanks

My Apology is due to those who, misled by promises which I had every expectation of being able to keep, have been long expecting the appearance of this volume

My Explanation of the delay in its publication is that, although nominally merely a new edition, the subject-matter has been rearranged and more than doubled in amount, and that not only by the incorporation of matter published since the appearance of the last edition, but also by the addition of the results of original experiments whenever the information on a particular subject appeared to be insufficient or of doubtful accuracy. In some cases these investigations have been progressing during the passage of the book through the press. A further cause of delay has been that I have discovered the maximum limit of my strength.

My Thanks are due to those chemists who have given me the benefit of their special experience in certain kinds of work, and by whose assistance some of the more important articles have acquired an almost exhaustive character. The names of those to whom I am indebted in this way are duly mentioned in connection with the sections in the revision of which they have assisted. My thanks are also due to those members of my staff who have conducted many of the experiments already referred to, and who have shown great zeal and often made valuable suggestions.

The arrangement of the subject-matter in numbered paragraphs has been abandoned as valueless. In the chapter on **FIXED OILS AND FATS** the specific gravities of bodies lighter than water are compared with water taken as 1000, in accordance with a widely-extended custom; but I have not realised any advantage from this mode of expression, and hence in the subsequent chapters the densities are compared with water taken as unity.

The growth of the subject-matter has compelled me to omit the

chapters on the AROMATIC ACIDS and TANNINS. They will form part of the Third and concluding Volume of the work, together with chapters on COLORING MATTERS, CYANOGEN COMPOUNDS, ORGANIC BASES, ALBUMINOIDS, &c. Much of the matter for this volume is already written.

ALFRED H. ALLEN.

SHEFFIELD, *October, 1886.*

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## FIXED OILS, FATS, AND WAXES.

*Ad. B. Bly* Pd

Under the names of fixed oils, fatty oils, fats, and waxes is classed a number of bodies occurring in animal and vegetable substances.

The term fixed or fatty oil is generally used for such members of the group as remain liquid at ordinary temperatures. Those having this character contain a relatively large proportion of olein or other fusible bodies, but beyond this there is no absolute distinction between fixed oils and fats.

The waxes possess well defined physical characters, and exhibit differences in chemical composition which distinguish them pretty sharply from the true fats. They are in many respects closely related to these, and are conveniently described in the same division.

The following are the general properties characterising the true fats and fixed oils —

1. When pure, they are mostly colorless or of a pale yellow color. Impure and commercial oils vary in color from light yellow to red, and even to brown and black. Many vegetable oils have a distinct shade of green from the presence of chlorophyl, and show absorption-spectra, which is never the case with oils of animal origin.

2. Their smell and taste are often peculiar, and are characteristic of their origin. As these characters become less perceptible the more completely the oil is purified, they may be due to the presence of associated and difficultly removable foreign matters, rather than to the constituents of the oil.

3. They are more or less unctuous, and if dropped in a liquid condition on paper they leave a permanent grease spot, unless they are crystalline and hard enough to be rubbed off.

4. They are not fluorescent and, as a rule, have no rotatory action on a ray of polarised light. Castor oil is sometimes optically active.

5. The specific gravity is less than that of water, varying between the limits of 875 and 970; but if certain anomalous oils from marine animals be excluded, the lowest density is about 912 at a temperature of 15° C. In the fluid state, at the temperature of boiling water, the

densities range from 850 to about 910. The waxes and allied bodies are, when molten, still lighter, their density ranging from 808 to 845.

6. The fusing or melting points vary within wide limits, and are liable to modification in an obscure manner by special treatment.

7. They are practically insoluble in water, but dissolve somewhat in absolute alcohol or strong spirit, especially when hot, and are readily soluble in ether, chloroform, carbon disulphide, benzene, petroleum spirit, turpentine, and other volatile solvents. They are readily miscible with one another.

8. The fixed oils and fats are composed of carbon, hydrogen, and oxygen, any nitrogen or sulphur existing in particular specimens being due to the presence of foreign matters. The chemical constitution is discussed in a separate section.

9. They are not inflammable at the ordinary temperature, but may be burnt by means of a wick. They are not capable of being distilled without decomposition. When heated alone they darken and evolve acrid offensive vapors; and when further heated to about  $315^{\circ}\text{C}$  ( $600^{\circ}\text{F}$ ) carbon dioxide is evolved, together with peculiarly irritating vapors of acrolein,  $\text{C}_3\text{H}_4\text{O}$ , various volatile organic acids, and gaseous, liquid, and solid hydrocarbons. The temperature at which these decompositions occur has been improperly called the "boiling point" of the oil, the phenomenon of apparent ebullition being really due to the escape of the gases formed by the decomposition. When caused to pass slowly through a red hot tube they are almost wholly decomposed into volatile products, consisting of carbon monoxide and hydrocarbons.

10. On distillation with superheated steam, they suffer a simpler decomposition, with formation of glycerol and fatty acids. This change may also be effected by acting on them with sulphuric acid or a strong base. The reaction is known as "saponification," and is discussed at length in another section.

11. If air be excluded, the fixed oils may be preserved unchanged for a lengthened period, but, on exposure to air, many of them thicken with absorption of oxygen, and are ultimately converted (if exposed in sufficiently thin layers) into a yellowish, transparent skin or varnish<sup>1</sup>. Such oils (*e.g.*, linseed, walnut, hempseed, and poppy-seed oils) are called drying oils.

12. The non-drying oils behave in a different manner on exposure

<sup>1</sup> Under certain conditions, as when cotton-waste, shoddy, or hemp is moistened with oil and exposed to the air, the oxidation of the oil becomes so energetic as to lead to considerable elevation of temperature, and even actual inflammation.

to air. When absolutely free from foreign matter most of them remain unchanged, but commercial specimens gradually turn *rancid*, that is, lose their color (and to a certain extent their fluidity), and acquire an acrid, disagreeable taste, and acid reaction to litmus paper. This alteration is due to the presence of foreign matters, such as the cellular substance of the animal or plant from which the oil was extracted. These bodies furnish nourishment for microbes which set free fatty acids, besides producing small quantities of volatile acids (*e g*, butyric, valeric, caproic) of strong odor. By agitating such rancid oil with hot water, and subsequently treating it with a cold and dilute solution of sodium carbonate, the products of decomposition may often be removed and the fat restored to its original state

## EXTRACTION AND PURIFICATION OF FIXED OILS AND FATS.

For the *extraction* of oils and fats from animal tissues it is often sufficient to allow the substance (*e g*, cod-liver) to become somewhat putrid, when some of the oil drains from it, or may be obtainable by slight pressure. A further quantity can be extracted by warming or boiling the tissue with water, as is done with blubber. In the case of lard and tallow it is merely necessary to heat the substance alone, and strain the melted fat away from the membranous matter. From compact tissue, such as bone, the whole of the fat can be extracted by a solvent only

The extraction of the fat or oil from vegetable tissues may be effected by boiling the crushed substance with water, or by subjecting it to powerful pressure, either at the ordinary temperature or between plates heated to a little beyond the fusing point of the fat. The product obtained in the last manner will usually contain more "stearin" or solid fat than the "cold drawn" oil. In either case a certain quantity of the fat is mechanically retained by the tissues, and hence a larger yield can be obtained by the use of carbon disulphide or petroleum spirit, which, on being distilled off, leaves the fat behind

The proportion of oil or fat yielded by any particular material depends on many conditions. According to Vohl, the average percentage of oil extracted by solvents from linseed is 27; from hempseed, 26; from poppy seed, 49; from walnuts, 50; and from almonds, 52 per cent. According to Voelcker, the proportion of oil in linseed varies from 31 to 38 per cent., the linseed cake containing from a little under 10 up to nearly 16 per cent.; while the oil in cottonseed

cake varies from 6 per cent in the undecorticated to 16 per cent. in the decorticated. Cacao-nibs contain on the average about 50 per cent of fat. Oils obtained by the use of solvents are more likely to contain impurities than those obtained by pressure.

### Determination of Oils and Fats.

In the laboratory, the determination of the oil in solid animal and vegetable matters is effected by treating the finely-divided and previously dried substance<sup>1</sup> with a suitable solvent under such conditions as to ensure complete extraction. Carbon disulphide or petroleum spirit may be employed for the purpose, but in the author's experience ether is more satisfactory, both from point of view of the health of the operator and the danger resulting from fire, due to breakage of the apparatus or other cause.

The *exhaustion* of seeds, bones, shoddy, oil-cakes, milk residues, &c., may be effected by simply digesting the substance with the solvent at the ordinary temperature, with frequent agitation, in a closed flask.

After some hours, the flask should be opened, placed in hot water, and the solvent thus raised to its boiling point. The liquid is then filtered into a weighed flask, and the residue washed with the solvent. The solution is subsequently evaporated or distilled by steam heat, and the residual oil weighed.

The foregoing method is unsatisfactory, as it requires a considerable quantity of the solvent, of which a notable proportion is likely to be lost. Hence an apparatus which will act automatically, and allow of complete exhaustion of the substance by a limited quantity of the solvent, possesses great advantages.

For this purpose, no better apparatus has been devised than that due to Soxhlet (fig 1). The substance to be exhausted of oil is enclosed in a plaited filter or cylinder of filter paper; or if it be coarse, it is sufficient to place it loose in a large test tube having an aperture at the bottom closed by a plug of glass-wool.

Thus arranged, the tube or filter with its contents is placed in a Soxhlet-tube, having a little glass-wool at the bottom,



FIG 1

<sup>1</sup> In the case of linseed and other substances containing drying oils, the distillation must either be omitted or conducted in an atmosphere of hydrogen or coal-gas.



and adapted by means of a cork to a flask containing the solvent. A vertical condenser is adapted to the upper end of the Soxhlet's tube, and the solvent kept boiling by a suitable source of heat. In the case of petroleum spirit, ether, or other volatile and inflammable solvent, this should be a tin vessel of water kept hot by a small flame. As the solvent boils it is condensed and falls on the substance to be extracted, remaining in contact with it until both the inner and outer tubes are filled to the level of the siphon, when the solution passes off into the flask, to be redistilled and recondensed, and so on until the process is judged to be complete. With a proper arrangement of the source of heat, the extraction goes on regularly and automatically. On changing the flask and replacing the inner tube by one containing a fresh sample, the apparatus is ready to be used for another extraction.

A very simple and convenient form of exhaustor, adapted either for extraction or reprecipitation, has been described by Dunstan and Short (*Pharm Jour*, [3] xiii 664). It consists of two glass tubes, the wider of which is drawn out at one end. The narrower and somewhat shorter tube fits into the outer one with much margin, and is also drawn out in such a way as to allow the end to protrude from the drawn out end of the wider tube when the smaller is inserted therein. At the point where the outer tube commences to contract it is indented on opposite sides, by which means two ledges are formed within the tube, which serve as supports for the narrower tube.<sup>1</sup> The inner tube serves to contain the substance to be exhausted. The lower drawn-out end of the wider tube is fitted by a cork to the flask containing the volatile solvent, while the upper end is connected with a condensing arrangement.

J. West-Knights has described (*Analyst*, viii. 65) a form of exhaustor which may be conveniently used when the quantity of material to be extracted is somewhat small (fig. 2). A percolator is made by cutting off the bottom from a test-tube of suitable size, and blowing a hole or two (AA) in the side of the tube about an inch from the top. A disk of filter paper or fine cambric (B) is tied over the lower end of the tube. The substance to be extracted is placed in the tube, and kept in its place by some glass wool or a perforated disc of metal, and the tube with its contents then fixed by a cork to the lower end of the tube of a vertical condenser (C). This is adapted by a larger cork (D) to the neck of an ordinary flask containing the volatile solvent.

<sup>1</sup> The indentations are made by pressing each side of the tube when red-hot with a pair of crocodile-tongs.

on heating which the vapor passes through the holes in the side of the test-tube up into the tube of the condenser, where it is liquefied. The condensed liquid drops back into the test-tube, percolates through the substance to be extracted, and falls to the bottom of the flask, to be again volatilised. As the percolator is inside the flask, its contents are kept constantly at the boiling point of the solvent, and, the action being continuous and automatic, very rapid exhaustion may be effected.

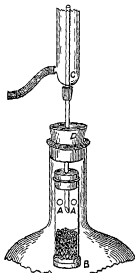


FIG. 2.

Other forms of exhaustor have been contrived by Church, Drechsel, Angell, Thoms, Thresh (*Pharm. Jour.*, [3] xv 281), and others, but those already described will be found sufficient for all purposes (see vol. i).

To recover the oil from its solution in the ether, or other liquid employed, the solvent should be distilled off at a steam heat, and the last traces of it removed by placing the flask on its side and heating it in the water-oven until constant in weight. In some cases the complete removal of the solvent is best effected by blowing a gentle stream of air,

previously filtered through cotton-wool, through the flask while it is maintained at a temperature of  $100^{\circ}\text{C}$ .

In the case of *liquids* containing oil in the form of emulsion, a separation can often be effected by agitation with ether. The extraction of the fat from milk can be effected in this manner if the liquid be previously made slightly alkaline.

For methods especially adapted to the determination of fat in milk, see volume iv.

### Purification of Oils.

The refining or purification of fixed oils is effected in various ways, according to their origin and the impurities it is desired to remove. The following is an outline of the methods of most general application. They may be modified in detail, or combined in a manner suited to any special case.

**ACTION OF LIGHT**—Simple exposure of a fixed oil to light for a period varying from a few days to as many months will often effect a

remarkable improvement. *Linseed and seal oils* afford good examples of the success of this treatment.

**ACTION OF HEAT**—By rapidly heating *palm oil* to about  $240^{\circ}\text{C}$ . ( $464^{\circ}\text{F}$ ), and maintaining it at that temperature for ten minutes, it is very effectually bleached, and the same is the case if poppy oil be kept at  $90^{\circ}$  to  $95^{\circ}\text{C}$  for four or five hours. The same treatment can be advantageously employed in other cases.

**FILTRATION**—Some oils are greatly improved by treatment with animal or wood charcoal. Kaolin, steatite, plaster of paris, and other substances may often be employed with advantages to effect a semi-mechanical clarification. After such treatment the oil usually requires filtration through canvas bags, which also serves to separate spermaceti, stearin, &c, deposited by cooling the oil. Clay is now very largely used for the clarification of oils.

**WASHING WITH WATER**—A very general method of purification consists in agitating the oil with water. This is often conveniently effected by driving in steam through a false bottom or perforated pipe. This treatment can be combined or alternated with any of the others, and, if desired, chemical reagents can be added to the water.

**TREATMENT WITH ACIDS**—A method of very general applicability, and one which, when carefully conducted, is remarkably efficacious, consists in violently agitating the oil, previously heated to about  $40^{\circ}\text{C}$ , if necessary, with from one to two per cent of concentrated sulphuric acid, which attacks and chars the impurities without materially affecting the oil. The acid is then allowed to settle, and the supernatant oil well washed with water; or steam is blown into the mixture for a short time, and the acid water allowed to separate from the oil. For 100 gallons of oil, about 10 lbs of sulphuric acid are usually required, diluted with an equal bulk of water. In some cases hydrochloric acid is substituted for sulphuric. Treatment with acid is very suitable as a means of refining most *seed oils* (e.g., rape and linseed oils), and greatly improves some of the fish oils, but the refined product is apt to contain traces of unremoved mineral acid, and an undesirable proportion of free fatty acids. These impurities are of no disadvantage if the oil is to be employed for soap-making, but acquire importance if it is to be used for burning or lubrication. Treatment with sulphuric or hydrochloric acid also serves to remove the lime which is present in *bone-fat*.

**TREATMENT WITH ALKALIES**—*Cottonseed oil, olive oil, sperm oil*, and some others, are advantageously purified by treatment with a solution of caustic soda, the quantity of which must be regulated

according to the proportion of free fatty acids and impurities present in the oil. *Cottonseed oil* contains a notable proportion of a resinous matter which produces a fine blue color with the alkali. The oil loses considerably in refining, and the proportion of alkali used should be regulated according to the indications of a preliminary laboratory trial. A specific gravity of 1.10 is a suitable strength for the ley. Cottonseed oil expressed in England from decorticated seed often contains so large a proportion of free acid that purification with alkali becomes practically impossible.<sup>1</sup>

Ammonia, sodium carbonate, magnesium carbonate, or milk of lime may sometimes be used with advantage to remove acids from oils. The use of alkali instead of acid for purification is to be preferred in the case of oils intended for use as lubricants or for cooking. The refined cottonseed oil now extensively used for cooking, &c., is remarkably free from acid.

**TREATMENT WITH OXIDISING AGENTS**—A remarkably effective means of clarifying certain *fish oils* consists in heating the liquid by means of steam to a temperature approaching the boiling point of water, and then blowing a current of air of a similar temperature through the liquid. The treatment must be cautiously conducted, or the rise of temperature may be so great as to cause a notable change in the density and viscosity of the oil, such as occurs purposely in the manufacture of "oxidised" or "blown oil."

Another very efficient oxidising agent, especially suitable for the treatment of *palm oil*, is chromic acid, as produced by the reaction of potassium dichromate with a suitable amount of sulphuric or hydrochloric acid. The oil is melted, strained if necessary, and then agitated at about 50° C with about 1 per cent of potassium dichromate previously dissolved in water. To this is added sufficient acid to react with the salt to form potassium and chromic chlorides or sulphates, a slight excess of acid being rather advantageous than otherwise. Some oils, when treated in this manner, retain chromium compounds with remarkable persistency.

**TREATMENT WITH REDUCING AGENTS**—In the case of *linseed* and *other drying oils*, exposure to light in contact with a deoxidising agent affords a very efficient means of clarification. Strips of metallic lead may be employed, or finely-divided precipitated lead, as recommended by Livache. A strong solution of ferrous sulphate also answers the

<sup>1</sup> The writer found a sample of oil from decorticated cottonseed expressed in Liverpool to require 14.1 per cent of KHO to neutralise the free acid. This corresponded to 70.5 per cent. of free acid calculated as oleic.

purpose, especially if assisted by exposure of the oil to light for some weeks, and accompanied with frequent agitation.

**TREATMENT WITH PRECIPITANTS.**—*Fish oils* and some others are greatly improved by violently agitating them with a hot solution of oak-bark or other *tannin-matter*. Steam and air can be blown in at the same time. After deposition, the clear oil should be treated with a solution of lead or aluminium acetate, to remove any excess of tannin, and is afterwards dried by treatment with plaster of paris. Other metallic solutions or reagents forming insoluble compounds with gelatin or albumin, may be employed with advantage in certain cases.

**PURIFICATION BY PRESSURE.**—This sketch of the principal methods of refining oils would not be complete without a reference to the widely applied use of hydraulic pressure for separating the solid from the liquid constituents of oils. The solid fats thus separated are commercially known as “*stearin*,” though they are frequently far from approximating to the pure ester of stearic acid. Similarly, the liquid expressed oils are conveniently termed “*oleins*,” though of very complex composition. The following are some of the chief instances in which commercial fats and oils are separated by pressure into solid and liquid portions —

<i>Original Oil.</i>	<i>Liquid Product</i>	<i>Solid Product</i>
Olive oil	Purified olive oil	Olive oil stearin
Cottonseed oil	Purified cotton oil	Cotton oil stearin
Coconut oil	Coconut olein	Coconut stearin
Tallow	Tallow oil	Tallow stearin
Lard	Lard oil	Lard stearin
Whale oil	Purified whale oil	Whale stearin
Sperm oil	Purified sperm oil	Spermaceti

## PHYSICAL PROPERTIES OF FIXED OILS AND FATS.

The general characters of the fixed oils have already been described. Some of their physical properties are of importance for their recognition and determination, this being especially true of their density, melting and solidifying points, absorption spectra, viscosity, and behavior with solvents. These characters, and the methods of observing them, are described in detail in the following sections.

Determinations of the refractive indices and electrical conductivities have been also proposed as methods of differentiating oils

### Cohesion-Figures of Oils.

The surface-tension of oils is a property which in certain cases is capable of useful application, though its value has been much exaggerated. To obtain the cohesion-figures which depend on the surface-tension, it is necessary to allow a drop of the oil to fall gently on the surface of still water contained in a flat evaporating-basin or soup-plate. In order to ensure success, and to obtain bold, well-defined figures, it is necessary that the vessel containing the water should be chemically clean; that the surface of the water should also be clean and free from organic matter, that the temperature should not be below  $15^{\circ}\text{C}$ ; and that the surface of the water should not be too limited. The time required to produce the characteristic figures should be carefully noted.

When a drop of *olive oil* is placed on the water, it slowly spreads out into the shape of a large disk with slightly recurved edges. The cohesion of the oil, however, soon causes the disk to contract, the edges first testifying the return of the cohesive force, a number of little spaces begin to appear round the edges, causing them to resemble a chaplet of beads. The spaces between the beads soon open out, and the edges become toothed, the detached portions in some parts reuniting themselves to the main sheet of oil, enclosing polygonal spaces bounded by fine beads and covered with an excessively fine dew of oil, which it requires a sharp eye to detect. This succession of changes occurs in about thirty-five seconds.

*Oil of sesame*, treated in the same manner, begins by forming a well-defined sheet. Contraction soon takes place, the final figure being a central spot with distinctly marked rays, between which other smaller rayed spots appear, the whole recalling the aspect of a spider's web loaded with dew. The phenomenon is complete in about sixty seconds.

Mixtures of olive with sesame oil give figures approaching more or less to the typical, according as one or the other is in excess. Other oils also give more or less characteristic cohesion-figures.

### Absorption-Spectra of Oils.

The absorption-spectra of the fixed oils occasionally afford valuable indications of their purity. For observing them a micro spectroscope may be used, but in many cases the light must be caused to pass through several inches of the oil to be examined. Although some vegetable oils give exceedingly striking absorption-bands, the position

of these is not capable of employment for their discrimination in many cases, as the absorption is not a property of the oils themselves, but of the chlorophyl and impurities contained in them. Hence the purification or clarification of an oil tends seriously to reduce the characteristic nature of the absorption-bands, which, indeed, may disappear altogether if the oil be long exposed to sunlight. In one particular, however, the absorption spectrum furnishes important information. Thus, no oils of animal origin give definite absorption-bands, the spectrum being merely obscured at the more refrangible end, whilst in many vegetable oils the absorption-bands of chlorophyl are exceedingly well marked, especially a band having about the same refrangibility as the Fraunhofer line B. By applying this fact it is easy to detect the presence of rape, olive, or linseed oil in sperm, cod, or lard oil. Castor and almond oil, on the other hand, give no well defined bands, and the band at B in the case of sesame oil is faint, though there is strongly marked absorption of the whole of the red nearly up to that point.<sup>1</sup>

### Viscosity of Oils.

A useful physical test for oils is based on their relative "body" or viscosity, a property which may be regarded as the converse of fluidity. The viscosity is usually compared with that of rape oil, but it may also be referred to water or glycerol as a standard.

The viscosity of an oil is determined by ascertaining the time a certain weight or measure takes to flow through a given aperture, but the results obtained vary not inconsiderably with the construction of the apparatus employed. The subject is fully discussed in the section on the "Examination of Lubricating Oils."

<sup>1</sup> The absorption-spectra of fixed oils of vegetable origin have been investigated by Doumer and Thibaut (*Corps Gras Industriels*), who classify them in the following manner —

- a. Oils exhibiting no absorption-spectrum, — sweet almonds, bitter almonds, castor
- b. Oils which absorb all rays of greater refrangibility than the green, but the spectra of which show no absorption lines, — colza, rape, mustard, and linseed
- c. Oils showing the absorption-spectrum of chlorophyl — olive, hempseed
- d. Oils, the (photographic) spectrum of which shows three broad bands in the more refrangible part, which bands are exactly in the position of the corresponding absorption-bands of chlorophyl, but the less refrangible bands characteristic of chlorophyl are wanting, — sesame, arachis, poppy, rape

These observations were made on the freshly expressed oils. They are not entirely in agreement with the statements made in the text, and it is evident that their practical value is seriously reduced by the change likely to be produced in the spectra by keeping, and by the different processes of refining which may have been employed.

### Specific Gravity of Fats and Fixed Oils.

The density of the fixed oils and fats is a property largely dependent on their constitution, and hence is more or less characteristic of each particular oil. As a rule, the specific gravity of different samples of the same kind of oil varies within very narrow limits, but it is liable to be affected by the treatment to which the oil may have been subjected in the process of refining, the presence of free fatty acids, the age of the oil and the amount of oxidation it has undergone, and by other circumstances.

The specific gravity of fixed oils may be ascertained by the usual methods, but great care is necessary. Owing to the high coefficient of expansion of oils the temperature at which the observation is made should be carefully noted, and in accurate determinations the thermometer employed should be an instrument the indications of which have been verified.

When a sufficient quantity of the sample is available, and results of extreme accuracy are not required, the determination of the density can be made very readily and satisfactorily by means of an accurate and delicate hydrometer. In any observations, save those of the roughest kind, the oil should be brought accurately to the standard temperature by immersing the hydrometer glass in water, cooled, if necessary, to 15.5° C. (60° F.) by dissolving in it sodium thiosulphate (hyposulphite) or ammonium nitrate. The hydrometer should be immersed in the oil for five or ten minutes, and the temperature again observed before taking a reading of the density, as the use of a warm hydrometer may cause an increase of several degrees in the temperature of the oil. Of course, in taking the density by a hydrometer, the accuracy of the instrument employed is presupposed, but many of the instruments sold are inaccurate to the extent of several degrees.

The specific gravity bottle and Sprengel-tube (see vol. I) may also be employed for ascertaining the densities of oils, and allow of more accurate determinations than can possibly be made with a hydrometer. The weight of distilled water which fills the bottle or tube at a temperature of 15.5° C. (60° F.) is usually (at least in England) taken as the unit of comparison in stating the density of fixed oils.<sup>1</sup>

As many of the fixed oils are solid or semi-solid at the ordinary temperature, their densities are not directly comparable with those of the fluid oils. This difficulty may be obviated by observing the spe-

<sup>1</sup> Oil merchants frequently use a hydrometer on which water is marked 0° and rape oil 28°.



cific gravity in a molten state at some higher temperature. This is done by Bell and Muter at 100° F. (37.8° C),<sup>1</sup> but C Estcourt has recommended that the determination be made at the boiling point of water. This may be done with a hydrometer or balance, if the cylinder containing the oil be kept for a sufficient time in boiling water before the reading is taken. A specific gravity bottle is less convenient, but with the Sprengel-tube high accuracy may be obtained. The weight of the Sprengel-tube and that of water contained at 15.5° C. being known, the tube should be completely filled with the oil, by immersing one of the outlets in the liquid and sucking at the other

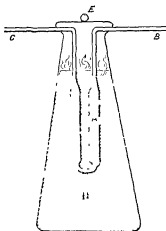


FIG 3

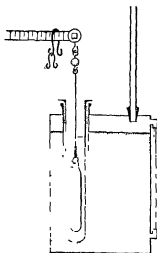


FIG 4

<sup>1</sup> Dr Muter gives the following figures for "actual densities" at 100° F of various oils, water at the same temperature being taken as 1000—

Olive oil, .	907 0	Linseed oil (boiled)	938 0
Almond oil, .	905 6	Caster oil, .	955 8
Arachis oil, .	908 5	Sperm oil, .	872 4
Rape oil, .	906 7	Whale oil, .	908 0
Nut oil, .	906 4	Seal oil, .	915 0
Cottonseed oil (brown)	917 6	Codliver oil, .	917 9
Cottonseed oil (refined),	913 6	Lard oil, .	907 8
Poppyseed oil, .	916 4	Neatsfoot oil, .	907 0
Hempseed oil, .	919 3	Margarine, .	903 to 906 0
Linseed oil (raw),	925 2	Butter-fat, .	912 to 916 0

These figures in most cases differ by 9 to 11 degrees from those expressing the densities of the same oils at 60° F (15.5° C)

The tube is placed in a conical flask containing water which is kept actively boiling, a porcelain crucible-cover being placed over the mouth of the flask. The oil expands and drops from the orifices. When this ceases, the oil adhering to the outside is removed by the cautious use of filter paper, the tube removed, wiped dry, cooled, and weighed. The weight of the contents divided by the weight of water contained at  $15.5^{\circ}$  will give the specific gravity at  $100^{\circ}$  C compared with water at  $15.5^{\circ}$  C. When the amount of material is sufficient, the determination may be made by use of the plummet, the use of which leaves nothing to be desired on the score of rapidity, accuracy, or ease of manipulation. In taking densities by the plummet at the boiling point of water, it is desirable to employ a cylindrical bath of metal (fig. 4), the top of which is perforated by two orifices. One of these is fitted with an upright tube, which serves to convey the steam away from the neighborhood of the balance, while into the other a test tube, 6 inches in length and 1 inch in diameter, fits tightly, the joint being made perfect by a ring of cork or india-rubber. The test tube is filled with the oil, the density of which is to be ascertained, and the plummet immersed in it. The water in the outer vessel is then kept in constant ebullition, until a thermometer, with which the oil is repeatedly stirred, indicates a constant temperature, when the plummet is attached to the lever of the balance, and counterpoised in the usual way (See also vol I for improved methods of determining specific gravity).

Hager has described an ingenious method of ascertaining the specific gravity of solid fats at the ordinary temperature. The fat is melted and drawn up into a pipette, from which it is allowed to drop slowly from the height of an inch into cold alcohol contained in a flat-bottomed dish, care being taken that each drop of fat falls in a different place. An alternative plan is to melt the fat in a small lipped capsule and allow drops of it to fall on a plate of glass which has been previously wiped with a wet cloth. On placing the glass in cold water the drops usually become detached on the slightest touch, but if necessary can be removed with a knife after half an hour. The fat globules obtained by one of the above methods are removed to a beaker containing dilute alcohol. The density of the liquid is then adjusted by addition of alcohol or water, till, after careful stirring, the fat-globules remain in equilibrium in any part of the liquid at a temperature of  $15.5^{\circ}$  C. Ammonia may be substituted for the spirit if preferred. The density of the liquid is then taken, and the result obtained recorded as the specific gravity of the suspended fat. The great

objection to this method is that fats and waxes which have undergone sudden cooling have abnormal specific gravities. On this account it is far preferable to employ for the experiment fragments which have been cut off a mass cooled under normal conditions.

The following table gives the densities, as determined in the author's laboratory, of a number of samples of oil at the temperature of boiling water. Some of the observations were made with the Sprengel-tube and others by the plummet; but in certain cases, where both methods were employed, the results showed such a close concordance that it is a matter of indifference, so far as the figures are concerned, which method is employed. In most cases the density of *the same sample* was taken at the ordinary temperature in addition, some of these latter observations being made by a hydrometer.—

NATURE OF OIL.	SPECIFIC GRAVITY OF OIL, WATER AT 15° C. (59° F.) BEING 1000	
	At 15° C. (59° F.)	At 98° to 99° C. <sup>1</sup> (208° to 210° F.)
Arachis oil, . .	922	867.3
Rape oil, . . . .	915	863.2
Neatsfoot oil, . . . .	914	861.9
Cottonseed oil, . . . .	925	872.5
Sesame oil, . . . .	931	867.9
Coconut olein, . . . .	926.2	871.0
Nigerseed oil, . . . .	927	873.8
Linseed oil, . . . .	935	880.9
Castor oil, . . . .	965.5	909.6
Whale oil, . . . .	930.7	872.5
Porpoise oil, . . . .	926	871.4
Seal oil, . . . .	924	873.3
Codliver oil, . . . .	927.5	874.2
Menhaden oil, . . . .	932	877.4
Sperm oil, . . . .	883.7	830.3
Bottlenose oil, . . . .	880.8	827.4

The next table shows the specific gravity at two different temperatures of various molten fats and other bodies which are solid at the ordinary temperature. The densities were ascertained by the plummet

<sup>1</sup> It will be observed that the densities in the third column of the foregoing table are recorded as obtained at a temperature of 98° to 99° C. In the author's laboratory water ordinarily boils at 99° C., and oil immersed in a vessel of boiling water rarely reaches a temperature exceeding 98.5° C.

method, and in each case the observations at the two different temperatures were made on *the same sample* of the substance. A column is added showing the difference in density corresponding to a change of  $1^{\circ}\text{C}$

NATURE OF FAT, &c	SPECIFIC GRAVITIES OF MILD FATS, &c, WATER AT $15.5^{\circ}\text{C}$ ( $60^{\circ}\text{F}$ ) = 1000		DIFFERENCE FOR $1^{\circ}\text{C}$
Palm oil,	893.0 at $50^{\circ}\text{C}$	858.6 at $98^{\circ}\text{C}$	717
Cacao butter,	892.1 " $50^{\circ}$	857.7 " $98^{\circ}$	717
Japan wax,	901.8 " $60^{\circ}$	875.5 " $98^{\circ}$	692
Tallow,	895.0 " $50^{\circ}$	862.6 " $98^{\circ}$	675
Lard,	898.5 " $40^{\circ}$	860.8 " $98^{\circ}$	650
Butterine,	898.2 " $40^{\circ}$	859.2 " $98^{\circ}$	672
Butter-fat,	904.1 " $40^{\circ}$	867.7 " $99^{\circ}$	617
Coconut stearin,	895.9 " $60^{\circ}$	869.6 " $99^{\circ}$	671
Coconut oil,	911.5 " $10^{\circ}$ <sup>1</sup>	873.6 " $99^{\circ}$ <sup>1</sup>	642
Palmnut oil,	911.9 " $40^{\circ}$ <sup>1</sup>	873.1 " $99^{\circ}$ <sup>1</sup>	657
Spermaceti,	835.8 " $60^{\circ}$	808.6 " $98^{\circ}$	716
Beeswax,	835.6 " $80^{\circ}$	822.1 " $98^{\circ}$	750
Carnauba wax,	850.0 " $90^{\circ}$	842.2 " $98^{\circ}$	975 <sup>2</sup>
Stearic acid (commercial),	850.0 " $60^{\circ}$	830.5 " $98^{\circ}$	750
Oleic acid (commercial),	903.2 " $15.5^{\circ}$	848.4 " $99^{\circ}$	656
Paraffin wax,	780.5 " $60^{\circ}$	753.0 " $98^{\circ}$	724

The figures in the foregoing tables represent merely the densities possessed by *particular samples* of different oils. The limits of variation of density, and the value of the specific gravity as a means of recognising and assaying the various fixed oils are discussed in a separate section.

**COEFFICIENTS OF EXPANSION OF OILS**—It is always desirable to determine the specific gravity of oils at the standard temperature, but in many cases in which this cannot be done a suitable correction may be made. It is evident that to ascertain the rate of expansion of an oil it is merely necessary to determine the density of a sample at two different temperatures, which should be as far apart as possible<sup>3</sup>. The

<sup>1</sup> The samples of coconut oil and palmnut oil were old, and had been frequently melted. Some time previously they showed densities notably less than the figures stated in the table.

<sup>2</sup> For obvious reasons, the rate of expansion of carnauba wax is only a rough determination.

<sup>3</sup> Thus a sample of rape oil was found to have a density of 915.0 at  $15.5^{\circ}\text{C}$ , and 863.2 at  $98^{\circ}\text{C}$ , the difference being 51.8. Dividing this by 82.5, the difference between the

rates of expansion of the molten fats, &c, are given in the table on last page, while from the figures recorded on p. 32 the writer has calculated the rates of expansion of various oils fluid at ordinary temperatures. The following table shows the values so obtained, together with certain determinations published by other observers —

NATURE OF OIL	CORRECTION FOR 1° C	OBSERVER	NATURE OF OIL	CORRECTION FOR 1° C	OBSERVER
Sperm oil,	618	A. H. Allen	Olive oil,	629	E. M. Stillwell
Bothering oil,	643	"	Arachis oil,	625	A. H. Allen
Whale oil,	607		Sassa oil,	620	"
"	722		Sesame oil,	621	"
Propane oil,	654	C. M. Wetherill	Cottonseed oil,	629	"
Sisal oil,	615	A. H. Allen	Coconut oil,	607	"
Shark liver oil,	649	"	Nigerseed oil,	627	"
Castor oil,	646	"	Linseed oil,	649	"
Mandelica oil,	654	"	Castor oil,	651	"
Nut-foot oil,	625				
Lard oil,	658	C. M. Wetherill			

From an inspection of the figures recorded in this and the preceding tables, it appears—(1) that the rates of expansion of fixed oils are not sufficiently different to be of any value for their recognition; (2) that of the fixed oils examined, all, with the single exception of whale oil, expand sensibly equally for equal increments of heat, or at least the figures obtained do not show greater variations than would probably be observed between different samples of the same oil, (3) that, with the exception of whale oil (the high figure for which is confirmed by an independent observer), the correction in density for fixed oils mentioned in the last table may safely be taken at 0.64 for each degree centigrade, or 0.35 for each degree Fahrenheit,<sup>1</sup> (4) the rate of expansion of the solid fats and waxes,

temperatures at which the observations were made ( $98.0 - 12.5 = 85.5$ ), the figure 0.626 is obtained as the correction to be made for a variation of 1° C from the standard temperature.

<sup>1</sup> Thus, if a sample of oil has been found to have a density of 0.907 at 22° C, the density at 15.5° C may be found in the following manner —

$$\begin{array}{r}
 .220 \\
 -15.5 \\
 \hline
 6.5 \times .64 = 4.16 \\
 + .9070 \\
 \hline
 .91165
 \end{array}$$

The establishment of the fact that the rate of expansion of the majority of fixed oils is practically identical, will greatly facilitate corrections for temperature in cases where it is not convenient to ascertain the density at exactly the standard point.

when in a molten state, is not ascertained with such a degree of accuracy as in the case of the oils liquid at ordinary temperatures, but in most cases is sensibly higher than that of the oils of which olein is a leading constituent, this difference extending to free stearic and oleic acids<sup>1</sup>

It is evident that the *coefficient of expansion* of an oil may be deduced by dividing the temperature-correction by the density. Thus the coefficient of expansion of olive oil will be  $\frac{.000715}{.918} = 0.000715$  for each degree centigrade

**Melting and Solidifying Points of Oils and Fats.**—The observation of the solidifying point of an oil is often of considerable importance, especially in the case of lubricating oils, in which too high a melting point is a decided disadvantage. Similarly, the suitability of the solid fats for many of the purposes to which they are applied is greatly dependent on their melting points.

Entire uniformity of solidifying or melting points for particular oils and fats is not to be expected, as in most cases the natural fats consist of a mixture of liquid and solid substances, the proportions of which may vary sensibly in different samples of what is nominally the same kind of oil. Moreover, the melting points, like the specific gravities of the natural oils and fats, are liable to obscure alterations by lapse of time, and are further modified by the presence of varying amounts of free acid. It has also been observed that many of the fats solid at the ordinary temperature have at least two distinct melting points. Thus the ordinary clarified tallow of commerce, if previously melted at a temperature considerably above its fusing point, shows a fusing point of 95° to 96° F. If it be carefully remelted at that temperature, cooled, and the melting point again taken, it will sometimes be found nearly 20° F. above the former determination.

In making observations of the melting and solidifying points of oils and fats it is absolutely necessary to get rid of any water or suspended matter. This is best effected by keeping the fat gently melted for an hour or two, and then filtering it through dry paper.

The following are the most satisfactory methods of ascertaining the melting points of oils and fats —

a The substance is melted at a temperature slightly above its fusing point, and while molten is drawn up into a very narrow glass tube

<sup>1</sup> Owing to the enormous contraction undergone by many waxes and fats in the act of solidification, in the solid state they are considerably denser than the fluid fixed oils. Thus, solid beeswax is as dense as castor oil, but in the molten state it is much the lighter of the two.

(made by drawing out one end of a piece of ordinary quill tubing), where it is allowed to solidify spontaneously. After an interval of *not less than one hour* the tube, open at both ends, is attached by a cork or india-rubber ring to the stem of a thermometer in such a manner that the part of the tube containing the substance of which the melting point is to be observed, shall be at the same level as, and in close proximity to, the bulb. The thermometer, with its attached tube, is then immersed in water, which is gradually heated at a rate not exceeding  $0.5^{\circ}\text{C.}$  per minute until fusion of the contents of the capillary tube takes place, when the thermometer is observed and the temperature recorded. The flame is then removed, and the temperature at which the fat resolidifies also observed. In cases in which the melting and solidifying points are not notably different, it is usual to record the mean of the two as the true melting point of the substance. It is desirable to immerse the beaker of water containing the thermometer in an outer vessel also filled with water, and to apply the source of heat to the latter. A half-liter flask, from which the neck has been cut off, filled to the brim (fig 5), furnishes a very convenient water-bath, and allows of a very regular and gradual heating of the water contained in the beaker placed in its mouth.

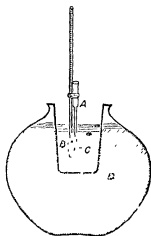


FIG 5

It is evident that, without some modification, the foregoing method is applicable only to bodies melting above the freezing point of water. By substituting strong brine for the water, however, much lower temperatures may be observed.

R. Bensemann (*Jour Soc Chem Ind*, iv 535) somewhat modifies the method last described. He places a drop of the previously melted fat in the wider part of a piece of quill-tubing drawn out to a capillary orifice. The fat is allowed to solidify completely, and the tube is then attached to a thermometer and placed in water which is gradually heated. The temperature at which the fat becomes sufficiently fluid to run down into the capillary part of the tube is called the point of incipient fusion, while the point of perfect fusion is that at which all

trace of turbidity disappears from the fat. In the case of fatty acids there is often a difference of  $3^{\circ}$  to  $4^{\circ}$  C. between the two points.

*b* When the fat of which the melting point is to be observed is not very fusible, the following method, due to Bevan and Cross (*Jour. Chem. Soc.*, xli 111), gives very satisfactory results. A very thin piece of sheet-iron (ferrotype plate) is cut into an elliptical form, about an inch long by half an inch wide. At one of the foci (A) a small depression is made, and at the other a hole (B) is cut, of such size as to allow the plate to be fixed on to the elongated bulb of a thermometer (C), so as to project therefrom at right angles. A glass float (D) is made by blowing a small bulb at the end of a capillary glass tube

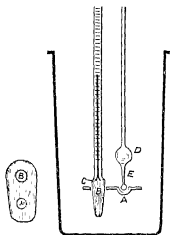


FIG. 6

about three inches long, a small looped or hoe-shaped piece of platinum wire (E) being sealed into the bulb at the end opposite the stem of the float. To make an observation, a very small quantity of the sample is melted in the indentation of the iron plate, and while still liquid the loop or hoe of the platinum wire of the float is immersed in it and allowed to become fixed by the spontaneous solidification of the substance, the stem of the float being supported in a vertical position. A thermometer is then cautiously introduced into the hole in the plate, and with it supported in a small beaker, which is then filled with

mercury or other liquid. This is then gradually heated till the substance under observation melts, when the float is released and instantly rises to the surface of the liquid. The results are very concordant, and free from certain sources of error to which observations made by the capillary-tube method are liable.

*c* The following plan is applicable within a greatly extended range of temperature.—Some clean mercury is placed in a small beaker, and a delicate thermometer immersed in the metal. A minute drop of the liquid fat or oil is then placed on the mercury. If the fat be easily fusible, the mercury is then cooled down by immersing it in iced water, or in a freezing mixture, until the drop of oil solidifies, the temperature at which the change of state occurs being noted. On



removing the outer bath containing the cooling agent, the mercury will gradually rise in temperature till the oil liquefies, and the temperature at which this occurs can be observed with great accuracy. In taking the melting points of the more infusible fats, there is no occasion to cool the mercury, which, on the contrary, is immersed in a beaker or neckless flask, filled with water to a higher level than the mercury. The water is heated very gradually till the fat is observed to become transparent and to spread over the mercury. The temperature at which this occurs is the liquefying point of the sample. The change of state is very readily observed, and several observations can be made simultaneously. The beaker containing the mercury may be advantageously covered with a funnel (through the neck of which the thermometer passes) to prevent cooling by currents of air.

d. A useful technical method of determining the *solidifying point* of waxes and fatty acids, and which may be used advantageously in various other cases, is as follows —A test-tube, about 5 inches in length by  $\frac{2}{3}$  inch in diameter, is fitted with a ring or collar of cork or india rubber, by which it is fixed in the mouth of an empty bottle or flask. The melted substance is then poured into the (warmed) tube till it is about two-thirds filled, and a delicate thermometer, previously warmed, is suspended freely in the liquid, so that the bulb may be wholly immersed. When the fat commences to solidify at the bottom of the tube the thermometer must be attentively observed. The operator then stirs the contents of the tube slowly, by giving the thermometer a circular movement, first three times to the right and then thrice to the left. The first effect of the agitation is to cause the thermometer to fall slightly, but subsequently a sensible rise takes place, and the mercury remains stationary for at least two minutes. The temperature thus indicated is the solidifying point of the substance, and the results obtained are remarkably constant. A rise of several degrees is often observed subsequently. In such cases both temperatures should be recorded. The above method is much used for commercial examinations under the name "titer test."

e. F. Rudolf, after testing various methods of determining the melting points of fats, finds that the most concordant results are obtained by covering a thermometer bulb with a layer of the fat about 3 mm. thick, immersing it in water which is gradually heated, and observing the temperature at which the fat begins to separate from the bulb and ascend through the water.

f. The solidifying points of some fats were determined by Rudolf by observing the temperatures at which they become solid whilst

violently agitated, but with such fats as exhibit a rise of temperature during solidification, it was found best to take as the solidifying point the temperature to which the thermometer rose during solidification.

The following table exhibits some of Rudorff's results —

SUBSTANCE	MELTING POINT BY METHOD <i>e</i> °C	SOLIDIFYING POINT BY METHOD <i>f</i> °C	THERMOMETER RISES DURING SOLIDIFICATION TO °C
Cacao butter, . .	33.5		27.4
Nutmeg butter, . .	70 to 80 (?)		41.7 to 41.8
Japan wax, . . .	50.4 to 51.0		50.8
Mutton suet, . .	46.5 to 47.4	32 to 36	} Several degrees
Beef suet, . . .	43.5 to 45.0	27 to 35	
Spermaceti, . . .	43.5 to 44.3	43.4 to 44.2	
Yellow beeswax, .	63.4	61.5 to 62.6	
White beeswax, . .	61.8	61.6	
Stearic acid, . . .	56.0 to 56.6	55.7 to 55.8	

A rise of temperature during solidification was observed in the case of artificial mixtures, as well as in that of the natural substances. It was exhibited by mixtures of spermaceti with stearic acid, and of paraffin with stearic acid, being probably due to the constantly varying composition of the liquid remaining after partial solidification.

The usual melting and solidifying points of many oils, fats, and waxes, are given in tabular form later.

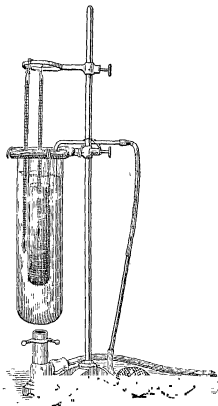
The following is the A. O. C. method for determination of melting point —

The materials required are — A piece of ice floating in recently boiled distilled water, and a mixture of alcohol and water of the same specific gravity as the fat to be examined. This is prepared by boiling separately distilled water and 95 per cent alcohol for ten minutes to remove the gases which they may hold in solution. While still hot, the water is poured into the test-tube described below until it is nearly half full. The test tube is nearly filled with the hot alcohol, which is carefully poured down the side of the inclined tube to avoid too much mixing. If the alcohol is not added until the water has cooled, the mixture will contain so many air-bubbles as to be unfit for use. These bubbles will gather on the disk of fat as the temperature rises and finally force it to the top.

The apparatus (fig. 7) consists of — A thermometer reading easily and accurately to tenths of a degree, a cathetometer for reading the thermometer (this may be done with an eyeglass if held steadily and properly adjusted), a thermometer, a tall beaker 35 cm. high and 10 cm. in diameter; a test-tube 30 cm. long and 3.5 cm. in diameter, a stand for supporting the apparatus, some method of stirring the water in the beaker (for example, a rubber blowing-bulb and a glass tube extending to near the bottom of the beaker).

The melted and filtered fat is allowed to fall from a dropping-tube from a height of from 15 to 20 cm. on a smooth piece of ice floating in distilled water.

that has been recently boiled. The disks thus formed are from 1 to 1.5 cm. in diameter, and weigh about 200 mg. By pressing the ice under the water the disks are made to float on the surface, whence they are easily removed with a steel spatula, which should be cooled in the ice-water before using. The test-tube containing the alcohol and water is placed in a tall beaker containing water and ice, until cold. The disk of fat is then dropped into the tube from the spatula and at once sinks to the part of the tube where the density of the diluted alcohol is exactly equivalent to its own. The delicate thermometer is placed in the test-tube and lowered until the bulb is just above the disk. In order to secure an even temperature in all parts of the alcohol mixture in the vicinity of the disk, the thermometer is used as a stirrer. The disk having been placed in position, the water in the beaker is slowly heated and kept constantly stirred by means of the blowing apparatus already described. When the temperature of the alcohol-water mixture rises to about  $6^{\circ}$  below the melting point, the disk of fat begins to shiver and gradually rolls up into an irregular mass. The thermometer is now lowered until the fat particle is even with the centre of the bulb. The bulb of the thermometer should be small, so as to indicate only the temperature of the mixture near the fat. A gentle rotatory movement should be given to the thermometer bulb. The rise of temperature should be so regulated that the last  $2^{\circ}$  of increment require about ten minutes. The mass of fat gradually approaches the form of a sphere, and when it is sensibly so the reading of the thermometer is taken. As soon as the temperature is taken the test-tube is removed from the bath and placed again in the cooler. A second tube, containing alcohol and water, is at once placed in the bath. The test-tube (ice



110 7

water having been used as a cooler) is of low enough temperature to cool the bath sufficiently. After the first determination, which should be only a trial, the temperature of the bath should be so regulated as to reach a maximum of about  $1.5^{\circ}$  above the melting point of the fat under examination. The edge of the disk should not be allowed to touch the sides of the tube. This accident rarely happens, but in case it should take place, and the disk adheres to the sides of the tube, a new trial should be made. Triplicate determinations should be made, and the second and third results should show a near agreement.

### Relations of Fixed Oils to Solvents.

Fats and oils are, without exception, wholly insoluble in *water* and *aqueous liquids* generally.

In *cold alcohol* the fixed oils are but little soluble, as a rule, and the solid fats and waxes still less so. In boiling alcohol, however, some of the fluid oils dissolve to a considerable extent, especially if the solvent be anhydrous. Quantitative statements respecting the solubility of oils in alcohol are, however, generally unreliable, the solubility recorded being, in many cases, merely a rough indication of the proportion of free fatty acid which happened to be present in the sample examined. The following statements cover all the general principles and reliable facts respecting the solubility of the fixed oils in alcohol:—

1. Those oils containing the esters of lower fatty acids (*e g*, porpoise oil, coconut oil, butter fat) exhibit exceptional solubility in alcohol.

2. Those oils containing the ester of linolic acid (*e g*, linseed and other drying oils) are comparatively readily soluble in alcohol.

3. Castor and croton oils dissolve with facility in alcohol, and are sharply distinguished by this character from the majority of oils.

In *ether*, *chloroform*, *carbon disulphide*, *benzene*, and oil of *turpentine* the fixed oils dissolve with great facility, being in many cases miscible with those solvents in all proportions.

*Petroleum spirit* acts, in the majority of cases, like the solvents just mentioned, but castor oil constitutes a remarkable exception to the general rule, being practically insoluble in petroleum spirit and other petroleum products (see "Castor Oil").

The behavior of various fixed oils with *glacial acetic acid* has been investigated by E. Valenta (*Dingl. polyt. J.*, cclvi. 296; *Jour. Chem. Soc.*, xlv. 1078). Equal parts of the oil and of glacial acetic acid of 1056.2 specific gravity are mixed,<sup>1</sup> and gradually heated with continuous shaking, until complete solution takes place or the acid begins

<sup>1</sup> i.e. of the sample of oil, previously melted if necessary at a gentle heat, and an equal measure of glacial acetic acid are convenient quantities to employ.

to boil. A thermometer is then immersed in the liquid, the tube allowed to cool slowly, and the temperature recorded at which the liquid becomes turbid. The writer has tried this test on a number of oils. He finds a slight variation in the strength or proportion of the acid employed is not of importance; and the temperature at which turbidity occurs with any particular specimen is readily observed and fairly constant. Unfortunately the writer's experience is not in accord with that of Valenta as to the turbidity-temperatures of particular oils, a fact that renders it probable that a more extended experience will prove that different specimens of the same description of oil give results showing considerable variations. The discordant figures obtained by Valenta and the writer for palm oil are probably due to the different proportions of free acid in the samples; and the same explanation probably applies to Valenta's figures for green and yellow olive oil.

The following table shows the results both of Valenta and the author —

KIND OF OIL.	TEMPERATURE OF TURBIDITY °C.	OBSERVER.	KIND OF OIL.	TEMPERATURE OF TURBIDITY °C.	OBSERVER.
Green olive oil, *	85	Valenta	Palm oil,	23	Valenta.
Yellow " "	111	"	Linseed oil,	26-27	"
Almond oil,	110	"	Neem butter,	27	"
Almond oil,	112	"	Cocunut oil,	40	"
" "	87	Allen	Linseed oil,	48	"
Apricot kernel oil,	114	Valenta	Bassia oil,	64.5	"
Nut-torn oil,	102	Allen	Butter-fat,	61.5	Allen
Sesame oil,	87	"	Porpoise oil,	40	"
" "	107	Valenta	"	"	"
Melonseed oil,	108	"	Palm oil,	83	"
Cottonseed oil,	110	"	Butterfat,	98	"
" "	"	"	Lard,	96.5	"
Neem-seed oil,	49	Allen	Beef tallow,	95	Valenta
Lime-seed oil,	57	"	Pressed tallow,	111	"
" "	"	"	Care to bottle,	105	"
Menhaden oil,	64	"	"	"	"
Cod-liver oil,	101	Valenta	"	"	"
" "	79	Allen	"	"	"
Shrimp-liver oil,	106	"	Oils & kernel oil,	Completely soluble at the ordinary temperature	Allen
Sperm oil,	98	"	Caster oil,		
Bottle-neck oil,	102	"	Colophony,		
" "	"	"	"	"	"
Rapeseed oil,	Not completely dissolved at the boiling point of acetic acid	Valenta	Stearic acid (commercial),	36	"
Mustard-seed oil,		"	Oleic acid (commercial),	27	"
White radish-seed oil,		"	"	"	"

From an inspection of the above table it would appear that olein is only with difficulty soluble in glacial acetic acid, and that the same is true of stearin. The discrepancy between the figure of Valenta and

that of the author for the turbidity temperature of palm oil makes the solubility of palmitin uncertain; but it is evident that the esters of fatty acids lower than palmitic (as contained in porpoise oil, butter fat, coconut oil, laurel oil, nutmeg butter, &c.) dissolve with comparative facility. The author obtained remarkably constant results from several samples of butter, and it appears probable that further experience may prove the method to afford a simple means of distinguishing butter from butterine. The incomplete solubility of rape oil and other oils from the *cruciferae*, even at the boiling point of acetic acid, is noteworthy, as are the low figures found for linseed oil, nigerseed oil, and menhaden oil, as compared with those for the non-drying oils.

Valenta has also proposed to employ glacial acetic acid at 50° C. for distinguishing mineral oils from rosin oil, the former being sparingly and the latter readily soluble in that reagent.

According to Pearman and Moot, a somewhat improved method of working this test is, instead of using an ordinary test tube, to use a short and somewhat thick test-tube into which a well fitting stopper has been ground. Into this tube is weighed 2.75 gm. of the fat, 3 c.c. of the acetic acid is then run in from a burette or other suitable arrangement. The tube is then stoppered and placed in a beaker of warm water, increasing the heat until, after well shaking the tube, the contents become quite clear. The source of heat is then removed, and the test tube so placed that it is in the centre of the beaker of heated water, and by means of a thermometer attached to the tube by a rubber band the whole is allowed to rest until the change from brilliancy to turbidity. The change is very definite and can be repeated over and over again with a maximum error of about 0.25° C.

## CONSTITUTION AND CHEMICAL PROPERTIES OF FATS, OILS, AND WAXES.

The fats, fixed oils, and waxes are esters of a series of acids mostly monobasic and called, from their sources, the fatty acids. The natural fats and fixed oils are all esters of the triad radicle, tritenyl,  $C_8H_6$ . Their composition may be expressed by the general formula  $C_8H_6A_3$ , in which A is a radicle of some acid. From the fact that the radicle  $C_8H_6$  occurs in glycerol, it is sometimes called *glycyl* or *glyceryl* and the esters are often called *glycerides*. The series that are mostly generally represented in the natural fats and oils are those having the general formulæ  $C_nH_{2n-1}O_2$  (stearic acid series);  $C_nH_{2n-2}O_2$  (oleic acid series);  $C_nH_{2n-3}O_2$  (linolic acid series);  $C_nH_{2n-4}O_2$  (ricinolic acid series). Tritenyl stearate,  $C_8H_6(C_{18}H_{35}O_2)_3 = C_{51}H_{110}O_6$ , is called tri-stearin, or, better, stearin, it is the chief constituent of mutton-fat

Similarly, olein is the principal component of almond, olive, and lard oils, and palmitin of palm oil. The esters of (homo) linolic and ricinolic acids respectively constitute the chief parts of linseed and castor oils. Olein and linolin, being liquid, are found most largely in the oils, while stearin and palmitin constitute the major portion of most fats.

With a few probable exceptions, the natural esters appear to contain three molecules of acid-radicle, but monostearate or monostearin, distearate or distearin, and similar bodies can be obtained by heating glycerol under pressure with the requisite proportion of fatty acid. Japan wax appears to be an example of a natural ester containing only two atoms of the acid-radicle,  $C_{15}H_{31}(\bar{A})_2OH$ , and the existence of other natural bodies of a similar kind is probable. In butter fat the molecule of tritenyl is probably united to different fatty acids.

The constitution of some of the natural fats and oils is still uncertain, and it is possible that some of them are the esters of homologues of tritenyl, or may have a constitution of a wholly different nature.

The waxes proper contain the esters of higher alcohols of the methyl series. Thus, spermaceti consists chiefly of cetyl palmitate,  $C_{15}H_{31} \cdot C_{16}H_{33}O_2$ , whilst Chinese wax, beeswax, and carnauba wax contain still higher radicles, and the last substance apparently a diatomic alcohol in addition. Sperm oil and bottlenose oil are chiefly composed of bodies having a constitution similar to that of the waxes.

In addition to the esters which constitute the essential portions, most natural fats, oils, and waxes contain more or less of free fatty acids, and small proportions of coloring, odorous, resinous, and other matters, to which the characteristic colors, smells, and tastes are mostly due. Small proportions of cholesterol are sometimes present, and the list of these principles will be much extended as research progresses.

**FREE FATTY ACIDS** in natural fats and oils are usually products of the decomposition, owing to the presence of mucilaginous or albuminous matters. Ordinary butter, which contains casein, readily turns rancid and contains free butyric acid; but if all casein and water be removed by melting and filtering the butter, the butter-fat may be kept unchanged for a long time. Over-treatment with sulphuric acid in the process of refining oils often results in the formation of free fatty acids. Commercial oils which have been refined by this process are apt to retain traces of free mineral acid.

The proportion of free fatty acids is best determined by titration in presence of alcohol with standard alkali and phenolphthalein.

The *proportion* of free fatty acids in commercial oils is often very

considerable—far larger than is commonly supposed. Thus, in palm oil the free acid, calculated as palmitic acid, usually varies from 12 to nearly 80 per cent. In eighty-nine samples of olive oil intended for lubricating use, L. Archbutt (*Analyst*, ix 171) found from 2.2 to 25.1 of free (oleic) acid, the mean being 8.05 per cent<sup>1</sup>. In the superior grades of olive oil the proportion of free acid is much smaller. In rape oil the percentage of free acid is generally from 1.5 to 6 per cent.; but cottonseed oil, which is refined by means of alkali, is generally free from any trace of acid<sup>2</sup>. The presence of free acid in an oil is doubtless the main, if not the only, cause of its tendency to act on metals, and therefore seriously affects the suitability of the oil for use as a lubricant. Burstyn found that the extent of the action of olive oil on brass was regularly and directly proportional to the percentage of the acid present. The subject is considered more fully in the section on "Lubricating Oils."

#### Saponification and Proximate Analysis of Fixed Oils.

*Fatty oils* heated with water under a pressure of 8 to 12 atmospheres, or distilled with superheated steam, are decomposed into fatty acids and glycerol. This method of decomposing fats is employed in the industrial production of fatty acids and glycerol.

Many natural oils and fats decompose into fatty acids and glycerol in presence of traces of albuminous or other foreign matter. The free fatty acids often present in commercial palm oil, olive oil, and tallow are due to this cause.

Decomposition occurs when a fatty oil is heated to 110° C, with about 8 per cent. of concentrated sulphuric acid. On washing the product with hot water, the sulphuric acid and glycerol are removed, and the fatty acids separate in the form of an oily layer.

Decomposition also occurs when a fat or oil is treated with basic oxides or hydroxides. The change occurs more readily with some oils than with others, and is promoted by heat and by using alcohol or glycerol as a solvent for the alkali. A salt (soap) of the fatty acid is produced, glycerol being likewise formed. The soaps produced by

<sup>1</sup> L. Archbutt found that free acid, if present in greater proportion than about 5½ per cent., unfitted olive oil for burning in railway lamps, the wick becoming charred.

<sup>2</sup> In a sample of porpoise oil which had been brought home in contact with the blubber, and which had drained therefrom at the ordinary temperature, the author found 9.02 per cent. of free oleic acid, and in oil (from the same cargo) extracted by boiling the blubber with water, the free acid amounted to 22.65 per cent.



potassium, sodium, or ammonium hydroxide are soluble in water, but most other soaps are insoluble<sup>1</sup>

Wax yields soaps and a monatomic alcohol, instead of glycerol. The decomposition is usually difficult, and a solution in alcohol or glycerol should be employed.

When an ester is split up into an acid and an alcohol, the change is called "saponification," no matter whether the agent effecting the change be water, an acid, or a base. The term is even extended to the decomposition of ethers which do not yield fatty acids. It is evident, therefore, that the saponification of fixed oils is a definite chemical reaction, precisely analogous to the decomposition of the ordinary salts.

ESTER	CHIEF SOURCES	FORMULA	MOLECULAR WEIGHT	PRODUCTS OF SAPONIFICATION OF 100 PARTS	
				FATTY ACID	GLYCEROL
Trityl butyrate (butyrum),	Butter-fat,	$C_8H_5(C_4H_7O_2)_3$	302	87.44	39.46
Trityl valerate (valerum),	Porpoise oil, whale oil,	$C_8H_5(C_5H_9O_2)_3$	344	88.96	26.77
Trityl laurate (laurum),	Coconut oil, palmnut oil,	$C_8H_5(C_{11}H_{21}O_2)_3$	638	94.04	14.42
Trityl palmitate (palmitum),	Palm oil, lard,	$C_8H_5(C_{16}H_{31}O_2)_3$	806	95.28	11.41
Trityl stearate (stearum),	Tallow, lard, cacao butter,	$C_8H_5(C_{18}H_{35}O_2)_3$	890	95.73	10.34
Trityl oleate (oleum),	Olive oil, almond oil, lard oil,	$C_8H_5(C_{18}H_{33}O_2)_3$	884	95.70	10.40
Trityl erucate,	Rape oil,	$C_8H_5(C_{22}H_{41}O_2)_3$	1052	96.30	8.75
Trityl linolate (linum),	Linseed and drying oils,	$C_8H_5(C_{19}H_{37}O_2)_3$	878	95.67	10.48
Trityl ricinolate (ricinum),	Castor oil,	$C_8H_5(C_{22}H_{41}O_2)_3$	932	95.92	9.68
Cetyl palmitate,	Spermaceti,	$C_{16}H_{33}C_{16}H_{31}O_4$	480	53.33	50.42
Myrcyl palmitate,	Beeswax,	$C_{20}H_{41}C_{16}H_{31}O_4$	676	37.87	64.79
Ceryl cerotate,	Chinese wax,	$C_{27}H_{55}C_{21}H_{43}O_4$	788	52.03	60.25
Dodecetyl oleate,	Sperm oil,	$C_{12}H_{25}C_{18}H_{33}O_4$	450	62.67	36.88
Dodecetyl decylate,	Bottlenose oil,	$C_{12}H_{25}C_{10}H_{21}O_4$	404	63.79	35.78

<sup>1</sup> The method of saponification now most extensively practised on a large scale consists

The foregoing table shows the composition of the leading proximate constituents of fats, oils, and waxes, and the theoretic proportions of fatty acid and alcoholic bodies resulting from their saponification —

It is seen that, with the exception of butyric and valeric, which are only found in small proportion in natural fats and oils, all the esters which form the proximate constituents of fats and oils yield nearly equal amounts of fatty acids on saponification, the amounts, if lauric be excepted, being constant within a range of about 1 per cent. Similarly the proportions of glycerol yielded range within comparatively narrow limits. Hence it may fairly be asserted that the majority of fats and oils yield, on saponification, from 95 to 96 per cent. of fatty acids, and about 10 per cent. of glycerol. The esters of butyric, valeric, or lauric acid contained in butter-fat, porpoise, and coconut oils respectively, yield a larger proportion of glycerol, while rape oil, containing an ester of erucic acid, yields a smaller proportion.

The waxes yield much smaller proportions of fatty acids, and, instead of glycerol, give large proportions of alcohols of the methyl series, as solid bodies insoluble in water. The nature and proportion of the products of saponification sharply distinguish the sperm and bottlenose oils from all other fixed oils of commercial interest.

The nature of the fatty acids produced on saponification is of importance in distinguishing the various fixed oils. Thus the drying oils yield chiefly linolic acid,  $C_{18}H_{32}O_2$ , or possibly a homologue,  $C_{19}H_{34}O_2$ , as a liquid product having a strong affinity for oxygen and combining with a large proportion of bromine or iodine, but not solidified by the action of nitrous acid. The non-drying oils mostly contain olein, which has comparatively little affinity for oxygen, and takes up less bromine or iodine than linolin, but is solidified by treatment with nitrous acid. Rape oil contains erucin, which is not solidified by nitrous acid, and has a very high molecular weight. All the foregoing and their homologues yield lead salts soluble in ether. On the other hand, the higher esters of the stearin series yield lead salts insoluble in ether, are solid at ordinary temperatures, and do not assimilate bromine or iodine. The acids derived from lower members of the series (e.g., butyric and valeric) are soluble in water, and some of them volatilise to a notable extent in a current of open steam. Butter-fat, porpoise and coconut oils contain esters of these soluble or volatile fatty acids and yield larger proportions of glycerol than most other fixed oils.

in treating the fat in a closed vessel with 2 or 3 per cent. of lime, and driving in steam at a pressure of 8 to 10 atmospheres. In some works magnesia or zinc oxide is substituted for the lime.

The proportions of *fatty acids* obtained from the various fixed oils fully bear out the foregoing theoretic views, but owing to the difficulty which, till recently, attended the accurate determination of glycerol, discordant statements have been made as to the proportion obtained, and various theories have been advanced to account for the supposed deficiency.

The following table gives the percentage of glycerol produced by the saponification of various oils and fats, as ascertained by the permanganate process (see "Glycerol").—

SUBSTANCE	GLYCEROL PER CENT		SUBSTANCE	GLYCEROL PER CENT	
	Benedikt and Zsigmondy	A. H. Allen		Benedikt and Zsigmondy	A. H. Allen
Douglas (Bottlenose) oil,		3.10	Olive oil,	10.1 to 11.4	9.52
Northern whale oil,		11.06	Rape oil,	"	9.14
Porpoise oil,		11.09	Sesame oil,		9.50
Mouhaden oil,		11.10	Cottonseed oil,	9.4 to 10.0	9.49
Lard,		10.83	Linseed oil,		9.14
Tallow,	9.9 to 10.0		Castor oil,		8.36
Butter-fat,	10.2 to 11.6	11.06	Oat-fat,		
			Coconut oil,	13.3 to 14.5	12.11
			Palmist oil,		11.70
			Palm oil, <sup>2</sup>		9.71
Beeswax,	none		Japan wax,	10.3 to 11.2	11.6 to 14.7
			Myrtle wax,		13.38

These figures are very instructive. They negative the statement of König, who could obtain no glycerol by saponifying oat-fat,<sup>2</sup> and but little from linseed oil. They also controvert the extraordinary assertions of Hammerbocker and Lehmann that coconut oil consists chiefly of free fatty acids. It actually yields more glycerol than the majority of oils, owing to the presence of laurin and other esters of comparatively low molecular weight.

<sup>1</sup> The palm oil contained a considerable quantity of fatty acid. The figures for bottle-nose, olive, rape, and sesame oils were obtained in the author's laboratory by the use of methyl alcohol, which experiment subsequently showed was not of satisfactory purity. Hence these results are probably somewhat in excess of the truth. The other figures of the author were obtained with aqueous potash, and have a tendency to be below the truth. Benedikt and Zsigmondy used methyl alcohol. Fox and Wanklyn recommend saponification in presence of ethyl alcohol, which would give excessive results, but they have not published any figures.

<sup>2</sup> The oat-fat analysed was prepared in the writer's laboratory by extracting oatmeal with ether. It contained free fatty acid corresponding to 46.3 per cent of oleic acid. The total fatty acids amounted to 95.18 per cent, and had a combining weight of 201.7.

The proportions of glycerol obtained in the author's laboratory by the analysis of Japan wax are higher than have been observed in the case of any other natural fat.

TO EFFECT SAPONIFICATION for general purposes of chemical analysis an alcoholic solution of caustic potash is by far the most convenient reagent. As the process is frequently employed, it is desirable to describe it once for all.

An alcoholic solution of alkali is prepared by dissolving 80 grm of good caustic potash in 1 litre of methylated spirit, which has been previously redistilled with a little caustic alkali. It is desirable to dehydrate the spirit by keeping it over a large excess of dry potassium carbonate. About 5 gm. of the clarified fat or oil are exactly weighed in a 4 oz wide necked flask, treated with 25 to 30 c.c. of the solution of alkali in spirit, and the flask closed with a cork fitted with a long tube. The flask is heated over boiling water, and as soon as the spirit boils the contents are mixed by circular agitation. In most cases the whole of the oil will rapidly disappear, forming a clear solution of soap, which may be further heated for a short time with occasional agitation, to ensure the complete saponification of the fat. The cork is then removed and the alcohol evaporated off. In the presence of unsaponifiable oil the contents of the flask should be allowed to boil until nearly dry, and the residue treated with 25 c.c. of spirit, and again boiled down. In cases where there is no danger of loss of hydrocarbon oils, or ethers of lower fatty acids, by incautious treatment, the saponification and subsequent evaporation can be satisfactorily conducted in a hemispherical porcelain basin, placed over a small naked flame. The mixture is well stirred with a glass rod, and kept gently boiling until the alcohol is nearly driven off and the residual liquid froths strongly. By this time the whole of the oil should have disappeared, but, if incomplete saponification be suspected, 10 c.c. of alcohol may be added, and the evaporation repeated. To ensure the saponification of butter-fat, codliver oil, the waxes, and other substances difficult to decompose, it is better to place the sample and alcoholic solution in a strong 200 c.c. bottle, closed by an india-rubber stopper firmly fastened by wire. The bottle is then kept at 100° C., and frequently agitated during half an hour, or until no globules of oil can be seen, when it is opened, and the contents rinsed into a basin and evaporated over boiling water till the alcohol is expelled. Special precautions for ensuring the saponification of waxes are described in the section on "Beeswax."

Considerable use is now made of a method of saponification by means of an alkaline glycerol solution, which permits of the employment of a high temperature and enables the saponification to be effected more rapidly and completely (See Alkali-glycerol Process)

**SEPARATION OF THE PRODUCTS OF SAPONIFICATION.**—The solution of soap, freed in the foregoing manner from alcohol, should then be diluted with warm water till it measures 70 to 80 c c. A perfectly clear solution will usually be obtained if a pure oil has been used and the process has been successfully conducted, but *waxes*, and mixtures containing *hydrocarbons* and other foreign matters, will give a solution containing solid matter, or oily globules in suspension. These admixtures may usually be removed and determined by agitating the soap solution in a glass separator, with an immiscible solvent, ether being the most generally suitable for the purpose<sup>1</sup>. The ethereal layer is then separated, evaporated, and the residue weighed. The best method of manipulation is described later. Cholesterol and other unsaponifiable matter are present in small proportion even in some of the purest fatty oils<sup>2</sup>.

If ether has been employed, it should be removed by keeping the soap solution at a gentle heat for some time. On then treating the solution with an acid, dilute sulphuric acid being generally preferable, a milky precipitate is produced, which, on warming the liquid, will collect into globules and form an oily layer on the surface. This layer consists of the *fatty acids* produced from the oil. These acids differ from the original esters in being soluble in alcohol, the solution having an acid reaction, and decomposing the carbonates of the alkali-metals, liberating carbon dioxide and forming soaps.

Fatty acids are, as a rule, almost wholly insoluble in water and not

<sup>1</sup> Owing to the limited solubility of myristyl alcohol in most solvents, the method described in the text is attended with practical difficulties in the case of beeswax and carnauba wax, though it is admirably adapted for the analysis of spermaceti. If the removal of the separated higher alcohol by an immiscible solvent be found impracticable, the solution of the soap should be treated with acetic acid in quantity just sufficient to destroy the pink coloration produced by phenolphthalein, and the solution precipitated by lead acetate. The precipitate should be washed, dried, mixed with sand, and the wax-alcohol dissolved by boiling petroleum spirit.

<sup>2</sup> In rigidly accurate experiments it is desirable to treat the unsaponified residue in the same manner as the original oil, as traces of fat are liable to escape saponification by a single treatment. If the residue left on evaporating the ethereal solution be treated with a little hot alcohol, the solution filtered hot, and the filtrate cooled, and, if necessary, allowed to evaporate spontaneously, crystalline plates of cholesterol will often be deposited. Wool fat contains a considerable proportion of cholesterol, and the writer has proved its presence, by the above method, in butter-fat, cod-liver oil, &c.

sensibly volatile at  $100^{\circ}$  C., but from butter-fat, coconut oil, palmtree oil, porpoise oil, and some others a notable amount of the lower fatty acids is obtained, and hence the acids from these sources are partially soluble in water, and capable of distillation with water at  $100^{\circ}$  C.

For obtaining these *soluble* or *volatile* acids from oils, the soap solution is acidulated with sulphuric acid in the manner already described, and the aqueous liquid separated from the layer of fatty acids, and the latter several times boiled with a considerable quantity of water in a flask furnished with a long tube or inverted condenser. The liquids resulting from these operations are separated from the *insoluble fatty acids*, which it is desirable to again boil with a moderate quantity of water, whilst driving a current of steam through the flask in which they are contained, collecting the distillate, and treating it like the washings<sup>1</sup>. The acidulated aqueous liquid first separated from the layer of fatty acids is then distilled to small bulk, and the distillate exactly neutralised with a standard solution of sodium, or barium, hydroxide, using phenolphthalein as an indicator. The first washings from the insoluble fatty acids are then added to the contents of the retort, and the liquid again distilled to a low bulk, the process being repeated with the succeeding washings. The different distillates obtained should be titrated separately with decinormal standard alkali and phenolphthalein, as, in this manner, with but little extra trouble, the progress and completion of the washing, &c., can be followed, and useful information obtained as to the probable nature and relative proportions of the *lower fatty acids* present.

The several neutralised distillates may now be united and evaporated gently to dryness, the residue being dried at  $100^{\circ}$  C till constant. It consists of the sodium or barium salts of the acids which passed over in the preceding distillation. If the total volume (in c.c.) of normal soda employed for the neutralisation be multiplied by 0.022, or the volume of normal baryta solution by 0.0675, and the number so obtained be subtracted from the gross weight (in grams) of the dry residue, the difference will be the weight of the *volatile fatty acids*. Their mean combining equivalent will be found by dividing their weight by the volume (in c.c.) of normal alkali required for their neutralisation.

A further examination of the volatile fatty acids can be made by

<sup>1</sup> When coconut or palmtree oil is treated in this manner, the distillate will be found to contain lauric acid, which, though almost insoluble in water, is volatile in a current of steam. It may be separated from the more soluble volatile fatty acids by filtering the distillate.

distilling the barium or sodium salts with phosphoric or diluted sulphuric acid, and examining the distillate as indicated in vol 1, p 485 *et seq.*

A very useful method of examining fatty oils for *volatile acids* has been devised by Reichert. It consists in distilling over an aliquot part of the acidulated solution of the saponified sample, and titrating the distillate with standard alkali. The details of the manipulation and the results yielded by different oils will be given later.

The foregoing method of isolating the lower fatty acids is not in practice so tedious as might be supposed; and in cases where the oil under examination is known not to contain any appreciable quantity of esters of the lower acids, the treatment for their isolation may be wholly omitted, and the *insoluble fatty acids* are practically identical with the *total fatty acids* liberated on adding a dilute mineral acid to the aqueous solution of the soap. The oily layer thus obtained should be shaken several times with warm water, or until, after separation, the aqueous liquid is no longer acid to litmus. The subsequent treatment of the *insoluble fatty acids* will depend on the nature and extent of the information required. In some cases it will be sufficient to add alcohol and titrate with standard alkali and phenolphthalein. If the fatty acids are to be weighed, the best mode of operating is to run them from the separator into a small paper filter previously wetted with hot water. The funnel containing the filter is placed in the mouth of a small dry beaker, and the whole heated in the water-oven. As the filter dries, the greater part of the fatty acids will pass through the paper into the beaker. When no more drops through, the funnel is removed to a small dry flask, and the acids adhering to the separator or other vessels removed by means of ether, carbon disulphide, or benzene. The solution thus obtained is poured into the filter and caught in the flask below. A fresh quantity of the solvent is used to effect complete solution and removal of the fatty acids from the filter, these washings also being allowed to run into the flask. The solvent is then distilled off by immersing the flask in hot water, and the residual fatty acids further dried by blowing a current of air through the flask till they begin to lose weight, or till all odor of the solvent has disappeared. The weight of fatty acids thus determined is added to that of the main quantity contained in the beaker, and the sum gives the *insoluble fatty acids* in the amount of fat employed for the analysis<sup>1</sup>. In most cases the determination of the *total*

<sup>1</sup> The method of treating the *insoluble fatty acids* described in the text possesses several advantages. Thus the greater part is at once obtained in a filtered and perfectly dry state.

insoluble fatty acids is sufficient, but, if desired, a further proximate analysis can be made by the methods indicated in the section on "Higher Fatty Acids."

The acidulated aqueous liquid remaining after the isolation of the insoluble fatty acids, and the removal of any volatile fatty acids by distillation, contains *glycerol*, which may be isolated by exactly neutralising the free acid with potash, evaporating the solution to dryness on the water-bath, and exhausting the residue with alcohol. On filtering and evaporating the alcoholic solution, the glycerol is obtained as a sweet syrupy liquid, which may be further purified by treatment with a mixture of alcohol and ether and evaporation of the filtered solution. Although glycerol resulting from the saponification of oils may be readily isolated in this manner, the results obtained are only very roughly quantitative, owing to the loss of glycerol during the several evaporations.<sup>1</sup> The determination of the glycerol produced by saponification is most accurately effected by determining the oxalic acid produced by its oxidation with permanganate, as described in the section on "Glycerol."

The following table shows in a condensed form the general process, just described, for the separation of the products of saponification of genuine fixed oils. The method of determining *foreign additions* to fixed oils is described in a separate section.

Saponify the oil, evaporate off the alcohol, dissolve the residual soap in water, and agitate the solution with ether			
ETHYREAL SOLUTION contains residues of, <i>hydrocarbons, unsaponified oil, and higher alcohols</i> (from waxes, sperm oil, &c.)	AQUEOUS LAYER. Acidulate with dilute sulphuric acid, and wash liberated fatty acids with boiling hot water		
	OILY LAYER consists of <i>insoluble fatty acids</i> , which may be converted into lead compounds, and these then treated with ether		AQUEOUS LIQUID on distillation gives—
	SOLUBLE IN ETHER Lead compounds of <i>oleic, ricinoleic, lauric, myristic, stearic, hypogaeic acids, &amp;c.</i>	INSOLUBLE IN ETHER Lead compounds of <i>myristic, palmitic, stearic, arachidic, erucic acids, &amp;c.</i>	IN DISTILLATE, <i>lower fatty acids</i> , such as <i>butyric, valeric, caproic, lactic, &amp;c.</i> estimated by titration with standard alkali, and further examined by fractional distillation, &c.
			IN RESIDUE, an aqueous liquid, which, when neutralised, carefully evaporated to dryness, and the residue treated with ether-alcohol, gives a solution of <i>glycerol</i> , left as a sweet syrupy liquid on evaporating the solvent, but which is more accurately determined in a separate portion by oxidation.

<sup>1</sup> Even if the distillation for removal of the volatile fatty acids be omitted, and every possible precaution be taken to avoid loss by volatilisation, the results are usually considerably below the truth.



**SAPONIFICATION EQUIVALENTS OF OILS.** Koettstorfer's Process — The saponification of fatty oils being a perfectly definite reaction, not only can the proportions of fatty acid and glycerol produced from any particular ester be calculated, but the proportion of alkali required for the saponification can be similarly ascertained from the general equation. —  $C_3H_5\bar{A} + 3KOH = C_3H_5(OH)_3 + 3K\bar{A}$  Conversely, if the proportion of alkali required to effect the saponification of a particular oil be accurately determined by experiment, the nature of the ester present can be inferred. From the above equation it appears that 1 molecule of a tritenyl ester requires 3 molecules of alkali for saponification. The number of parts saponified by 1 molecule of alkali will therefore be one-third of the molecular weight, but in the case of the ester of a monatomic alcohol, the number will be identical with the molecular weight. This figure, which really represents the number of grams of an oil saponifiable by one equivalent in grams of any alkali, or, in other words, the number of grams of an oil which would be decomposed by 1 litre of a normal solution of any alkali, is conveniently designated the "saponification equivalent" of an oil, and may in all cases be found by dividing the percentage of potassium hydroxide (KHO) required for saponification into 5610, or the percentage of sodium hydroxide into 4000. The expression of the neutralising power of oils in saponification equivalents has the advantage of being applicable to the results of saponification by any alkali, whilst the percentages of caustic potash required for complete saponification are not directly comparable with the figures obtained if soda be the alkali employed.

The following table shows the application of both modes of expression to the chief esters occurring as constituents of the natural fats and oils. As already stated, the saponification-equivalents of the monatomic esters are identical with their molecular weights, while those of the tritenyl esters are one third of their molecular weights —

SUBSTANCE	CHIEF SOURCES	PERCENTAGE OF CAUSTIC POTASH (KHO) REQUIRED FOR SAPONIFI- CATION	SAPONIFI- CATION EQUIVALENT.
Butyru, . . . .	Butter-fat, . . . .	55 73	100 67
Valerin, . . . .	{ Porpoise, dolphin, and whale oils, . . . }	48 92	114 67
Laurin, . . . .	{ Coconut and palm- nut oils, . . . }	26 38	212 67
Palmitin, . . . .	Palm oil, lard, . . .	20 88	268 67
Stearin, . . . .	{ Tallow; lard, ca- cno butter, . . . }	18 91	296 67
Olein, . . . .	{ Olive, almond, and lard oils, . . . }	19 04	294 67
Eruca, . . . .	Rape oil, . . . .	16 00	350 67
Linolin, . . . .	{ Linseed and other drying oils, . . . }	21 20	264 67
Isolinolin, . . . .	Linseed oil, . . . .	19 17	292 67
Ricinolin, . . . .	Castor oil, . . . .	18 06	310 67
Cetyl palmitate, . . . .	Spermaceti, . . . .	11 69	480
Myrcyl palmitate, . . . .	Beeswax, . . . .	8 30	676
Ceryl cerotate, . . . .	Chinese wax, . . . .	7 12	788
Dodecetyl oleate, . . . .	Sperm oil, . . . .	12 47	450
Dodecetyl doglate, . . . .	Bortienose oil, . . . .	12 09	464

These figures show that very striking and characteristic differences exist between the saponification equivalents of the various bodies. In practice, however, it rarely happens that an oil consists of a single ester in a state even of approximate purity, and hence the saponification equivalents of the natural oils are the resultants of the equivalents of their constituent bodies, and the quantitative value of the determination is reduced. Nevertheless, the peculiarity of constitution of many of the natural fats and oils may still be recognised in the following table, which gives the percentages of caustic potash required by, and the saponification equivalents of, a large number of samples. The table contains results obtained by Koettstorfer (K.), F. W. and A. F. Stoddart (S.), L. Archbutt (LA.), E. Valenta (V.), R. Moore (M.), Hubl (H.), O. Hehner (H.), W. H. Deering (D.), and the author (A.). In many instances the figures are the average or extreme results yielded by the examination of a large number of samples. A further experience of the process will doubtless show that the limits stated in the table in many instances require modification.

SUBSTANCE	OBSERVER.	NO OF SAMPLES	PERCENTAGE OF KHO FOR SAPONIFICATION	SAPONIFICA- TION EQUIVALENT
A-OILS--				
Lard oil,	S		19.1 to 19.6	285 to 286
Olive oil, . . .	K, S, V	80	19.1 to 19.6	
Olive oil,	L.A.	40	18.87 to 19.25	
Almond oil (sweet),	V	2	19.47 to 19.61	
Arachis oil, . . .	V, M	1	19.13 to 19.60	
Tea oil, . . .	Davies,	1	19.55	
Sesame oil,	V, M, A	3	19.00 to 19.24	
Cottonseed oil,	S, D, V, M, A.	8	19.10 to 19.66	
B RAPE OIL CLASS--				
Colza and rape oils,	K, D, S	8	17.08 to 17.90	318 to 330
Rape oil,	L.A.	44	17.02 to 17.64	
Mustardseed oil,	V	1	17.4	
Cabbageseed oil, .	Davies	1	17.52	
C VEGETABLE DRYING OILS -				
Linseed oil,	S, D, M, L.A.	9	18.74 to 19.52	286 to 300
Poppyseed oil,	V, M	2	19.28 to 19.46	
Hempseed oil, .	V	1	19.31	
Walnut oil, . . .	V	1	19.60	
Nigerseed oil, . .	S.	2	18.9 to 19.1	
D MARINE OILS--				
Codliver oil, . . .	A, V	2	18.61 to 21.32	250 to 303
Menhaden oil, .	A	1	18.20	
Pilchard oil, . . .	S	2	18.6 to 18.75	
Seal oil, . . .	S, D.	4	18.9 to 19.6	
Southern whale oil,	D	1	19.41	
Northern whale oil,	S, A	4	18.55 to 22.44	
Porpoise oil,	A	2	21.63 to 21.58	
E BUTTER CLASS--				
Butter-fat,	K, V, M, A.	large	22.15 to 23.24	241 to 253
Coconut oil, . .	V, M.	5	24.62 to 25.94	209 to 255
Palmnut oil, . .	V	1	22.00 to 24.75	
F STEARINS, AC -				
Lard, . . .	K, V, A	7	19.20 to 19.65	277 to 294
Tallow, . . .	K, D	9	19.32 to 19.60	
Dripping, . . .	M, A	2	19.65 to 19.70	
Margarine,	M, A	large	19.95 to 19.65	
Goose fat, . . .	V	3	19.20	
Beef fat, . . .	V, L.A.	2	19.09 to 19.71	
Palm oil, . . .	M, V	3	19.63 to 20.23	
Cacao butter, . .	V	1	19.36	
G FLUID WAXES--				
Sperm oil,	S, D, A	10	12.34 to 14.74	380 to 454
Bottlenose oil,	A, L.A, D	5	12.30 to 13.40	419 to 456
H SOLID WAXES--				
Spermaceti,	H	3	12.78 to 13.04	432 to 441
Beeswax,	H, H.L, A	large	9.2 to 9.7	.
Carnauba wax,	H, V, H, L.A	4	7.90 to 8.61	
I UNCLASSIFIED--				
Shark-liver oil,	A.	6	14.00 to 19.70	284 to 400
Wool fat (suet),	V	1	17.00	330
Olive-kernel oil,	V	1	18.85	258
Castor oil,	S, D, A, V,	6	17.00 to 18.15	309 to 319
Japanese wood oil,	Davies,	1	21.1	255
Japan wax,	H, H.L, V, A.	8	21.01 to 22.25	292 to 297
Myrtle wax,	D, A	2	20.67 to 21.17	265 to 273
Blown rape oil,	L.A, A	3	19.8 to 20.4	275 to 284
Colophony,	H, A, D	4	17.0 to 19.3	290 to 330

On inspecting the results recorded in the foregoing table, it appears that the members of Group A, consisting of olein with comparatively little stearin or palmitin, neutralise appreciably equal quantities of potash, whether of animal or vegetable origin. On the other hand, the members of Group B, all of which are derived from cruciferous plants, neutralise sensibly less alkali than those of Group A, a fact which is explained by the presence of a considerable proportion of the ester of erucic acid, or other higher homologues of oleic acid. In the case of the drying oils, the saponification equivalents are not characteristic, but they point to the probability of linolic acid having a higher molecular weight than that commonly attributed to it. The marine animal oils, Group D, do not yield very characteristic results, except in contrast with the figures of Group G, the members of which do not contain terephenyl, but consist essentially of esters of monatomic alcohols. Porpoise oil is remarkable for the notable proportion of valerine contained in it, and hence for its comparatively high neutralising power.<sup>1</sup> Of the solid fats, those of Group E resemble porpoise oil in containing esters of lower fatty acids, and hence possess lower saponification equivalents than the oils of Group F, which consist essentially of variable mixtures of palmitin, stearin, and olein.

The peculiar constitution of the true waxes (Group H) is indicated by their limited power of neutralising alkali, while the figures recorded for the unclassified oils are equally instructive, and are discussed at greater length in the special sections dealing with these bodies.

As hydrocarbon oils do not react with alkali, the proportion of these oils in admixture with fatty oils can be deduced from the amount of alkali requisite for the saponification of the sample. Thus, if a sample of so-called linseed oil require only 9.5 per cent. of KHO for its saponification, instead of 19.0 per cent., it may be assumed to contain 50 per cent. of hydrocarbon oil.

*The Determination of the Saponification Equivalent* of an oil is best effected in the manner described by Koettstorfer (*Zeits. Anal. Chem.*, 1879, p. 199), who applied it originally to the analysis of butter. The following are the details of the operation.—About 2.5 gm. of the sample, accurately weighed, are treated with 25 c.c. of approximately seminormal solution of potassium hydroxide in alcohol,<sup>2</sup> in a flask

<sup>1</sup> An ester of valerine acid also exists to a considerable extent in whale oil, blackfish oil, and dolphin oil. Chevreul obtained from the last-named oil as much as 20.9 per cent. of valerine acid.

<sup>2</sup> The alcohol employed for making the solution should be previously dehydrated by keeping it over an excess of dry potassium carbonate. Methylated spirit may be used if it be first distilled with a little caustic potash.

fitted with a long vertical tube. The flask is heated on the water-bath for about half an hour, or until complete solution of the fat takes place, and the saponification is judged to be complete. The operation is greatly expedited by subjecting the contents of the flask to frequent agitation. One c.c. of an alcoholic solution of phenolphthalein is then added, and the liquid titrated with seminormal hydrochloric acid; 25 c.c. of the potassium hydroxide solution, very carefully measured, should then be similarly treated without addition of fat, and titrated with hydrochloric acid in the same way as before. The difference between the volumes of standard acid used in the two testings gives the number of cubic centimetres corresponding to the alkali neutralised in saponifying the oil. Each cubic centimetre of seminormal hydrochloric acid ( $= 18.25$  gm HCl per litre) thus employed represents 0.02805 of KHO, whence the *percentage of potassium hydroxide* required to saponify the oil can readily be ascertained. The *saponification equivalent* of the oil is found by dividing the weight of the sample employed, expressed in milligrams, by the number of cubic centimetres of normal (not seminormal) acid corresponding to the alkali neutralised by the oil. If the percentage of potash required be known, the saponification equivalent can be found by dividing this percentage into 5610.

A further refinement of Koettstorfer's process consists in ascertaining separately the amounts of alkali required for neutralising the free fatty acids and for saponifying the neutral esters of the sample. A notable instance of the value of this mode of examination is the assay of beeswax by Hehner's method. It should always be employed when a wax or other substance difficult to saponify is under treatment.

In employing this method of examining fatty oils, it is necessary to use alcoholic alkali as free as possible from color, as any yellow or brownish tint materially affects the delicacy of the acid-reaction with phenolphthalein, under favorable conditions, the change from pink to yellow is very sharply marked. Carbonic acid, however, seriously influences the reaction; and hence the saponification and titration should be conducted with as little access of air as possible. It is absolutely necessary to ascertain the strength of the alcoholic alkali from day to day, as such solutions rapidly alter, and the mere heating is liable to cause a slight change in the neutralising power. Standard sulphuric acid cannot be conveniently substituted for the hydrochloric acid recommended for the titration, as its employment causes a precipitation of sulphate, which masks the end of the reaction.

**DISTILLATION PROCESS.**—A useful method of examining fats and oils consists in determining the amount of alkali required to neutralise the *volatile fatty acids*. This method of examination is due to Hehner and Angell, and was developed by Reichert, by whose name it is usually known. Its value has been fully confirmed, but as the process is an arbitrary one, only about four-fifths of the entire volatile fatty acids obtainable from butter being found in the distillate under the conditions of operation, it is necessary to adhere to the following procedure:—Saponify 2.5 gm. of the fat with 25 c.c. of approximately seminormal alcoholic potassium hydroxide, by heating it in a closed bottle or flask fitted with a long tube, as described on page 56. Transfer the product to a porcelain basin, and evaporate off the alcohol *completely* at a steam heat. Dissolve the residual soap in water, add dilute sulphuric acid in slight excess, dilute the liquid with water to 75 c.c., add some fragments of pumice coiled round with platinum wire, and distil gently till 50 c.c. have passed over. Filter the distillate, if not quite free from white flakes or oily globules, wash the filter with a little hot water, and titrate the clear solution with decinormal caustic alkali, using phenolphthalein as an indicator<sup>1</sup>. The number of c.c. of  $\frac{N}{10}$  alkali required is called the “Reichert number” of the substance.

The following table shows the results yielded by several substances when assayed by the distillation process. In the first column of figures is given the number of centimetres of decinormal alkali required to neutralise the volatile acids in the distillate from 2.5 gm. of oil, and in the second the parts of potassium hydroxide neutralised by the distillate from 100 gm. of oil. The second number is obtained by multiplying the first by 0.2244.

It is evident that the fats of milk (butter-fats) are distinguished from nearly all other fats by the large proportion of esters of the soluble volatile fatty acids. The most remarkable exception is that of porpoise oil, and sometimes whale oil; from the former the writer obtained 5 per cent. and Chevreul as much as 9.63 per cent. of valeric acid. Valerin appears to replace in porpoise butter the butyrin of the butter of terrestrial mammals.

<sup>1</sup> When the acidulated soap from coconut or palmnut oil is distilled, a notable proportion of lauric acid passes over and solidifies in the condenser or on the surface of the distillate. This should be removed by filtration, or the distillate will be found to neutralise so large a volume of alkali as considerably to diminish the practical value of the process, especially as a means of distinguishing butter from butter-substitutes. By adding water to the contents of the retort, again distilling, and repeating this process several times, a very considerable proportion of volatile fatty acids can be obtained from coconut oil.

SUBSTANCE.	CMC CENTIMETRES OF $\frac{N}{10}$ ALKALI REQUIRED	KHO REQUIRED BY 100 c.c. OF OIL	OBSERVER
Butter- or Milk-fat, Cow's, . .	12.5-15.2	2.80-3.41	Reichert, Cald- well, Moore, Allen, &c.
" " Ewe's, . .	13.7	3.07	Schmitt
" " Goat's, . .	13.6	3.05	"
" " Porpoise's, . .	11.3	2.51	Allen
Coconut oil, . . . . .	3.5-3.7	0.78-0.83	Reichert, Moore, Allen
Palmnut oil, . . . . .	2.4	0.54	Allen
Palm oil, . . . . .	0.8	0.18	Moore
Cacao butter, . . . . .	1.6	0.36	"
Margarine, . . . . .	0.2-1.6	0.04-0.36	Caldwell, Moore, Allen
Whale oil, . . . . .	3.7	0.83	Allen
" " " " " " " " " "	12.5	2.80	"
Porpoise oil, . . . . .	11-12	2.47-2.69	"
Sperm oil, . . . . .	1.3	0.29	"
Bottlenose oil, . . . . .	1.4	0.31	"
Menhaden oil, . . . . .	1.2	0.27	"
Codliver oil, . . . . .	1.1-2.1	0.24-0.47	"
Sesame oil, . . . . .	2.2	0.48	"
Cottonseed oil, . . . . .	0.3	0.07	Moore
Castor oil, . . . . .	1.4	0.31	Allen

Messl employs double the quantity of fat (5 gm) for the determination, and obtains a figure about 2.2 times as great as that of Reichert Wollny (*J S C I*, 1887, 831) has pointed out the following sources of error in the process — (1) Absorption of carbon dioxide during the saponification, introducing an error up to 10 per cent, (2) formation of esters during the saponification, causing a loss of 8 per cent, (3) formation of esters during the distillation, with a possible loss of 5 per cent, (4) coherence of the fatty acids during distillation, which may, in some cases, involve loss up to 30 per cent, (5) the form and size of the distillation apparatus and the rate of distillation, which may influence the result to the extent of 5 per cent.

The following official process of the A. O. A. C. is essentially the method as recommended by Wollny. The extent, however, to which the results may be influenced by the above mentioned sources of error has been shown to be greatly overestimated.

#### APPARATUS AND REAGENTS

*Sodium hydroxide solution* — One hundred gm of sodium hydroxide are dissolved in 100 c.c. of distilled water. The sodium hydroxide should be as free as possible from carbonates, and be preserved out of contact with the air.

*Alcohol*, of about 95 per cent, redistilled with sodium hydroxide.

*Acid* — Solution of sulphuric acid containing 25 c.c. of strongest sulphuric acid in 1000 c.c. of water.

*Barium hydroxide*—An accurately standardized, approximately decinormal solution of barium hydroxide

*Indicator*—One gram of phenolphthalein in 100 c c of alcohol

*Saponification flasks*, of from 250 to 300 c c capacity, of hard, well-annealed glass, capable of resisting the tension of alcohol vapor at 100° C

*Pipette* graduated to deliver 40 c c

*Distilling apparatus*

*Burette*—An accurately calibrated burette, reading to tenths of a cubic centimetre

#### DETERMINATION

*Weighing the fat*.—The butter or fat to be examined should be melted and kept in a dry, warm place, at about 60° for two or three hours, until the water and curd have entirely settled out. The clear, supernatant fat is poured off and filtered through a dry filter-paper in a jacketed funnel containing boiling water. Should the filtered fat, in a fused state, not be perfectly clear, it must be filtered a second time.

The saponification flasks are prepared by thoroughly washing with water, alcohol, and ether, wiping perfectly dry on the outside, and beating for one hour at the temperature of boiling water. The flasks should then be placed in a tray by the side of the balance and covered with a silk handkerchief until they are perfectly cool. They must not be wiped with a silk handkerchief within fifteen or twenty minutes of the time they are weighed. The weight of the flasks having been accurately determined, they are charged with the melted fat in the following way:—

The pipette with a long stem, marked to deliver 5.75, is warmed to a temperature of about 50°. The fat, having been poured back and forth once or twice into a dry beaker in order to thoroughly mix it, is taken up in the pipette and the nozzle of the pipette carried to near the bottom of the flask, having been previously wiped to remove any adhering fat, and 5.75 c c of fat are allowed to flow into the flask. After the flasks have been charged in this way they should be re-covered with the silk handkerchief and allowed to stand fifteen or twenty minutes, when they are again weighed.

*Saponification*—Ten c c of 95 per cent alcohol are added to the fat in the flask, and then 2 c c of the sodium hydroxide solution. A soft cork stopper is now inserted in the flask and tied down with a piece of twine. The saponification is then completed by placing the flask upon the water- or steam-bath. During the saponification, which should last one hour, the flask should be gently rotated from time to time, being careful not to project the soap for any distance up to its sides. At the end of an hour the flask, after having been cooled to near the room temperature, is opened.

*Removal of the alcohol*.—The stoppers having been laid loosely in the mouth of the flask, the alcohol is removed by dipping the flask into a steam-bath. The steam should cover the whole of the flask except the neck. After the alcohol is nearly removed, frothing may be noticed in the soap, and, to avoid any loss from this cause or creeping of the soap up the sides of the flask, it should be removed from the bath and shaken to and fro until the frothing disappears. The last traces of alcohol vapor may be removed from the flask by waving it briskly, mouth down, to and fro.



*Dissolving the soap* —After the removal of the alcohol the soap should be dissolved by adding 100 c.c. of recently boiled distilled water, warming on the steam-bath with occasional shaking until solution of the soap is complete.

*Setting free the fatty acids* —When the soap solution has cooled to about 60° or 70°, the fatty acids are separated by adding 40 c.c. of the dilute sulphuric acid solution mentioned above.

*Melting the fatty acid emulsion* —The flask should now be stoppered as in the first instance, and the fatty acid emulsion melted by replacing the flask on the steam-bath. According to the nature of the fat examined, the time required for the fusion of the fatty acid emulsion may vary from a few minutes to several hours.

*Distillation.* —After the fatty acids are completely melted, which can be determined by their forming a transparent oily layer on the surface of the water, the flask is cooled to room temperature, and a few pieces of pumice-stone added. The pumice-stone is prepared by throwing it, at a white heat, into distilled water, and keeping it under water until used. The flask is now connected with a glass condenser, slowly heated with a naked flame until ebullition begins, and then the distillation continued by regulating the flame in such a way as to collect 110 c.c. of the distillate in, as nearly as possible, thirty minutes. The distillate should be received in a flask accurately marked at 110 c.c.

*Titration of the volatile acids* —The 110 c.c. of distillate, after thorough mixing, are filtered through perfectly dry filter-paper, 100 c.c. of the filtrate poured into a beaker holding from 200 to 230 c.c., 0.5 c.c. phenolphthalein solution added, and decinormal barium hydroxide run in until a red color is produced. The contents of the beaker are then returned to the measuring flask to remove any acid remaining therein, poured again into the beaker, and the titration continued until the red color produced remains apparently unchanged for two or three minutes. The number of cubic centimetres of decinormal barium hydroxide required should be increased by one-tenth.

*Alkali-glycerol method* —The following process, originally devised by Leffmann and Baum for the saponification of butter and butter substitutes, is applicable to fats and waxes generally and will be found accurate and convenient. The statement made by some of the members of the A. O. A. C. that the glycerol is liable to be converted into salts of volatile acids has been disproved by several investigators.

The following reagents are required —

*Glycerol-soda* —One hundred gram of pure sodium hydroxide are dissolved in 100 c.c. of distilled water and allowed to stand until clear. Twenty c.c. of this solution are mixed with 180 c.c. of pure concentrated glycerol. The mixture can be conveniently kept in a capped bottle holding a 10 c.c. pipette with a wide outlet.

*Sulphuric acid.* —Twenty c.c. of pure concentrated sulphuric acid made up with distilled water to 100 c.c.

*Barium hydroxide* —An approximately decinormal, accurately standardized solution of barium hydroxide.

*Indicator* —An alcoholic solution of phenolphthalein.

In the case of butter, about 50 gram of the sample are placed in a beaker and heated to a temperature of 50° to 60° C. until the water and the curd have

settled to the bottom. The clear fat is then poured on a warm dry, plated filter and kept in a warm place until 25 or 30 c c have been collected. If the filtrate is not perfectly clear, it should be reheated for a short time and again filtered.

A 300 c c flask is washed thoroughly, rinsed with alcohol and then with ether, and thoroughly dried by heating in the water oven. After cooling, it is allowed to stand for about fifteen minutes and weighed. A pipette, graduated to 5.75 c c, is heated to about 60° C and filled to the mark with the well-mixed fat, which is then run into the flask. After standing for about fifteen minutes, the flask and contents are weighed. Twenty c c of the glycerol soda are added and the flask heated over the Bunsen burner. The mixture may foam somewhat, this may be controlled and the operation hastened by shaking the flask. When all the water has been driven off, the liquid will cease to boil, and if the heat and agitation be continued for a few moments complete saponification will be effected, the mixture becoming perfectly clear. The whole operation, exclusive of weighing the fat, requires less than five minutes. The flask is then withdrawn from the heat and the mixture dissolved in 135 c c of water. The first portion of water should be added drop by drop and the flask shaken between each addition in order to avoid foaming. When solution has taken place, 5 c c of the dilute sulphuric acid are added, a piece of pumice dropped in, and the liquid distilled until 110 c c have been collected. The condensing-tube should be of glass and the distillation conducted at such a rate that the above amount of distillate is collected in thirty minutes.

The distillate is usually clear, about 0.5 c c of the phenolphthaleïn solution are added and the standard barium hydroxide run in from a burette until a red color is produced. If the distillate is not clear it should be thoroughly mixed, filtered through a dry filter, and 100 c c taken, the reading of the burette being increased by one-tenth.

A blank experiment should be made to determine the amount of decinormal alkali required by the materials employed. With a good quality of glycerol this will not exceed 0.5 c c.

### Bromine and Iodine Absorptions of Fixed Oils.

Another method of differentiation based on the chemical constitution of the fats and oils is the determination of the amount of bromine or iodine taken up under conditions intended to ensure the formation of additive compounds only. The fatty acids of the acetic series are saturated bodies, and do not form additive compounds with iodine or bromine, while the acids of the acrylic series combine with *two* atoms and those of the propolic series with *four* atoms, as expressed by the following equations.—

Stearic Acid,  $C_{18}H_{36}O_2$ , does not combine with bromine or iodine.

Oleic Acid,  $C_{18}H_{34}O_2$ , forms  $C_{18}H_{34}Br_2O_2$ , and  $C_{18}H_{34}I_2O_2$ .

Linolic Acid,  $C_{18}H_{32}O_2$ , forms  $C_{18}H_{32}Br_4O_2$ , and  $C_{18}H_{32}I_4O_2$ .

Linolenic Acid,  $C_{18}H_{28}O_2$ , forms  $C_{18}H_{28}Br_6O_2$ , and  $C_{18}H_{28}I_6O_2$ .

The esters of the acids of these series behave similarly, so that a determination of the percentage of bromine or iodine assimilated gives a measure of the proportion of olein against palmitin and stearin in a fat, and of the luolin of a drying oil as compared with the olein of a non-drying oil.

**BROMINE-ABSORPTIONS** have been determined by Mills, Snodgrass, and Akitt (*Jour. Soc. Chem. Ind.*, ii. 435; iii. 366), the method of operating ultimately adopted being briefly as follows:—About 0.1 gm of the oil, previously deprived of all trace of moisture by heating or filtration through paper, is placed in a stoppered bottle of about 100 c.c. capacity, and dissolved in 50 c.c. of carbon tetrachloride, previously dried by calcium chloride. An approximately decinormal solution (8 gm. per litre) of bromine in dry carbon tetrachloride, having an exactly known strength, is then added gradually to the solution of oil, until there is, at the end of fifteen minutes, a permanent coloration. This is compared with a coloration similarly produced in a blank experiment, and thus a measure of the bromine-absorption is obtained. If great accuracy be desired, an excess of bromine may be used, aqueous solution of potassium iodide and starch added, and the solution titrated back with a standard solution of sodium thiosulphate; or the excess of bromine may be determined by titrating back with a standard solution of  $\beta$  naphthol in carbon tetrachloride, which reacts with bromine in the ratio  $\text{Br}_2 : \text{C}_{10}\text{H}_8\text{O}$ .

When the brominated product has a yellow color, as happens with some fish oils, the point at which the bromine is in excess is best observed through a solution of neutral potassium chromate.

**IODINE-ABSORPTIONS** have been determined by Baron Hubl (*Dingl. Polyt. Jour.*, ccliii. 281; *Jour. Soc. Chem. Ind.*, iii. 641), who, for several reasons, prefers this estimation to that of the percentage of bromine assimilated. When employed alone, iodine reacts very slowly, and hence Hubl uses an alcoholic solution of iodine in conjunction with mercuric chloride, in the proportion of 1 molecule ( $\text{I}_2$ ) of the former to at least 1 ( $\text{HgCl}_2$ ) of the latter. It is prepared by dissolving 25 gm of iodine in 500 c.c. of nearly absolute alcohol (free from fusel oil), and 30 gm of mercuric chloride in an equal measure of the same solvent. The latter solution is filtered, if necessary, and then added to the tincture of iodine. The mixed solution should be allowed to stand for twelve hours before being used, as, owing to the presence of impurities in the alcohol employed, it is liable to undergo considerable reduction in strength, and must in all cases be restandardised immediately before or after use. The strength is ascertained by titration

with decinormal solution of sodium thiosulphate, which in its turn is set by a solution of resublimed iodine in the usual way. The mercurial iodine solution reacts with ease at ordinary temperatures on either free unsaturated fatty acids or their esters to form chloro-iodo-addition products, the total proportion of halogen assimilated being estimated in terms of iodine.

To determine the iodine absorption, from 0.2 to 0.3 gram. of drying oil, 0.3 to 0.4 of non-drying oil, or from 0.8 to 1.0 gram. of fat, should be weighed accurately, and dissolved in 10 c.c. of chloroform. The solution is mixed in a stoppered flask with 20 c.c. of the standard solution of iodo-mercuric chloride, and if the liquid is not quite clear after agitation a further addition of chloroform is made. If the mixture becomes decolorised, or nearly so, after standing a short time, a further addition of 5 or 10 c.c. of iodine solution must be made. To ensure accurate results, the excess of iodine must be considerable, and hence the liquid ought still to be quite brown after standing for two hours.<sup>1</sup> After that time, from 10 to 15 c.c. of a 10 per cent aqueous solution of potassium iodide should be added, and the whole diluted with about 150 c.c. of water. The free iodine, part of which exists in the aqueous and part in the chloroformic solution, is then determined by titration with thiosulphate, the contents of the flask being frequently agitated, and starch solution being added just before the end of the reaction. A blank experiment with the same quantities of chloroform, iodine solution, &c., is made side by side with the actual test, so as to correct for any impurities in the reagents and to ascertain the true strength of the iodine solution. The difference between the volume of thiosulphate used in the blank experiment and that required in the experiment in which the oil was employed is then calculated into its equivalent of iodine, and this to units per cent. of the oil.

The product formed by the action of iodo-mercuric chloride on pure oleic acid is a greasy substance, which is colorless at first, but gradually turns brown from liberation of iodine. Determinations of the chlorine and iodine, as also of its saponification equivalent, show the compound to be a chloriodostearic acid of the formula  $C_{18}H_{31}IClO_2$ . The similar products formed by the action of the iodine solution on

<sup>1</sup> Hübl found that with free fatty acids the reaction is complete with only a small excess of iodine, but with fats or oils a larger excess must be employed, or the results will be too low. In presence of a sufficient excess of iodine, variations in the concentration of the fatty solution and in the amount of mercuric chloride present do not affect the results. The reaction should be allowed to continue for at least two hours (or, according to Aichbutt, six hours).

fats and oils are colorless, viscous, or resinous masses, which in general resemble the original substances. In order to render the whole of the iodine available, the presence of mercuric chloride in a ratio not less than  $\text{HgCl}_2 : \text{I}_2$  is essential.

The following table shows most of the results of Mills, Hubl, and others in juxtaposition. The bromine-absorptions found by the first chemist have been calculated into the equivalent percentages of iodine, so as to allow of more ready comparison with the direct iodine absorptions of Hubl and others. The iodine-absorptions can be calculated into the equivalent percentages of olein by multiplying them by the factor 1.152. Later and more accurate figures for the iodine absorption of various oils will be found in the tables of properties of oils.

SUBSTANCE.	BROMINE- ABSORPTION, PER CENT MILLS	IODINE-ABSORPTION, PER CENT		
		127 50 Br-Absorption	Hubl	Other Observers
Almond (sweet),	53.7	85.3	97.5-98.9	98.1*
Almond (bitter),	26.3	41.8		
Peach-kernel,	25.4	40.1		
Apricot kernel,	70.0†	111.1†	99-102	
Olive-kernel,			81.8	
Olive,	54.0-60.6	85.9-96.4	81.6-84.5	83.0*
Earth-nut (Arachis),	46.2	73.1	101-105	87.4*
Rape,	69.4	110.4	97-103	101-104*†
Sesame,	17.4	75.2	105-108	102.7*
Cottonseed,	50.0	79.5	106-108	106-109*†
Poppyseed,	56.5	89.9	135-137	131.0*
Nigerseed,				132.9†
Linseed (raw),	76.0	130.8	156-160	155.2*
Linseed (boiled),	103.4	163.8	118	
Castor,	58.3	92.7	81.0-81.7	84.3†
Menhaden,				117.9†
Cod-liver,	81.6-86.7	129.5-137.6		
Ling-liver,	82.4	131.0		
Seal,	57.3-59.9	91.2-95.3		
Whale,	50.9	80.9		
Bottlenose,	48.7	77.4		80.1†
SpERM,				84.3†
Nerfish-foot,			66.0	71.4†
Palm,	34.8-35.4	55.3-56.3	50.4-52.4	50.3*
Coconut,	5.7	9.1	8.9	8.9*
Cacao-butter,			31.0	
Japan wax,	1.5-2.3	2.4-3.7	4.2	
Butter-fat,	24.5-27.9	38.9-44.4	26.0-35.1	19.5-35.0*
Margarine,	36.3-39.7	57.7-63.1	55.3	50.0*
Lard,	37.3	59.3	59.0	61.9*
Tallow,			40.0	
Beeswax,	0.0-0.54	0.0-0.86		
Caruaiba wax,	33.5	53.3		

\* R. W. Moore. † L. Archbutt. ‡ T. Maben.

These figures indicate that the drying oils assimilate the largest proportions of the halogens, and this capacity might be employed as a measure of their drying power.

Hubl states that chemically pure oleic acid assimilates from 89.8 to 90.5 per cent of iodine, the theoretical proportion required for the reaction  $C_{18}H_{34}O_2 + I_2 = C_{18}H_{32}I_2O_2$  being 90.07 per cent. On the other hand, most of the non-drying vegetable oils assimilate a notably larger proportion of iodine than corresponds to the percentage of olein present, and the difference cannot in all cases be attributed to the presence of linolin or its homologues. Mills states that olive oil, purified by filtration after long deposition in the cold, washing, and drying over oil of vitriol, assimilated 54.0 per cent. of bromine, against 54.3 per cent theoretically required to form the brominated compound  $C_{18}H_{32}(C_{18}H_{30}Br_2O_2)_2$ .

Hubl's figures, showing a lower iodine absorption for boiled than for raw linseed oil, have been confirmed by later investigations. R. Williams (*Analyst*, 1895, 276) gives the following figures for boiled linseed oil —

	THIN	THIN	STOUT	VERY STOUT
Iodine absorption,	175.1 per cent	163 per cent	99.5 per cent	96.9 per cent.

**Acetyl Value** — The determination of acetyl value proposed by Benedikt is based upon the principle that hydroxy acids, on being heated with acetic anhydride, exchange the hydrogen atom of their hydroxyl group or groups for the radicle of acetic acid. The determination is carried out by heating the free fatty acids with acetic anhydride. (See under "Fatty Acids.") Lewkowitsch has pointed out several objections to this method and recommends a method based upon treatment of the original oil or fat. The procedure is as follows —

Boiled with an equal volume of acetic anhydride for two hours in a round-bottomed flask attached to an inverted condenser, the mixture is then transferred to a large beaker, mixed with several hundred c.c. of water, and boiled for half an hour. A slow current of carbon dioxide should be passed into the liquor through a finely drawn-out tube reaching nearly to the bottom of the beaker, this is done to prevent bumping. The mixture is allowed to separate into two layers, the water is siphoned off, and the oily layer again boiled out in the same manner until the last trace of acetic acid is removed. This is ascertained by testing with litmus paper. The acetylated product is freed from water and finally filtered through filter paper in a drying oven.

This operation may be carried out quantitatively, and in that case the washing is best done on a weighed filter. On weighing the acetylated oil or fat, an increase of weight would prove that assimilation of acetyl groups has taken place. This method may be found useful to ascertain preliminarily whether a notable amount of hydroxylated acids is present in the sample under examination.

Two or 4 grm. of the acetylated substance are saponified by means of alcoholic potash solution as in the determination of the saponification value. If

the "distillation process" be adopted it is not necessary to work with an accurately measured quantity of standardised alcoholic potash. In case the "filtration process" be used, the alcoholic potash must be measured exactly. (It is, however, advisable to employ in either case a known volume of standard alkali, as one is then enabled to determine the saponification value of the acetylated oil or fat.) Next the alcohol is evaporated and the soap dissolved in water. From this stage the determination is carried out either by the (a) "distillation process" or (b) "filtration process."

(a) *Distillation Process*—Add dilute sulphuric acid (1:10), more than sufficient to saturate the potash, and distil as usual in Reichert's distillation process. Since several one hundred c.c. must be distilled off, either a current of steam is blown through the suspended fatty acids or water is run into the distilling flask, from time to time, through a stoppered funnel fixed in the cork, or any other convenient device is adopted. It will be found quite sufficient to distil over 500 to 700 c.c., as the last 100 c.c. contain practically no acid. Filter the distillates to remove any insoluble acids carried over by the steam, and titrate the filtrates with decinormal potash, phenolphthalein being the indicator. Multiply the number of c.c. by 5.61 and divide the product by the weight of substance taken. This gives the acetyl value.

(b) *Filtration Process*—Add to the soap solution a quantity of standardised sulphuric acid exactly corresponding to the amount of alcoholic potash employed and warm gently, when the fatty acids will readily collect on the top as an oily layer. (If the saponification value has been determined, it is, of course, necessary to take into account the volume of acid used for titrating back the excess of potash.) Filter off the liberated fatty acids, wash with boiling water until the washings are no longer acid, and titrate the filtrate with decinormal potash, using phenolphthalein as indicator. The acetyl value is calculated in the manner shown above.

Both methods gave identical results; the latter will be found shorter.

The acetyl value indicates the number of milligrams of KOH required for the neutralisation of the acetic acid obtained on saponifying 1 gm. of the acetylated fat or wax.

In the case of those oils and fats which have a high Reichert value the apparent acetyl value would be too high, owing to the presence of the volatile acids. This influence will, to a greater extent, affect the distillation process than the filtration process. To eliminate this error, determine the volatile acids of the original oil or fat in precisely the same manner, and deduct the value thus obtained from the apparent acetyl value.

It should be noted that in the case of a fat containing free alcohols (phytosterol, cholesterol), or, in the case of waxes, the acetyl value will be a measure of both the hydroxy acids and the free alcohols. If present, acetic acid radicals are also absorbed by them. If the free alcohol is isolated its acetyl value may be determined as well. The difference between the acetyl value of the fat or wax and the acetyl number proportionate to the amount of free alcohol present will be the true measure of the hydroxy acids.

If a free alcohol is acetylated, no complication through formation of anhydrides can arise, and in that case simply the saponification value of the acetylated product—the acetate of the alcohol—is determined. This value is also the acetyl

value of the alcohol (the saponification value of the original alcohol being *nil*)

No	1 KIND OF OIL.	2 ACETYLATED OIL OR FAT			3 NEUTRALISED FILTRATE FROM III ACIDIFIED AND DISTILLED ACETYL VALUE CALCULATED	4 INSOLUBLE FATTY ACIDS FROM 3 DISTILLED AND USED FOR NEUTRALISING DISTILLATE DECIMOMAL KOH
		Saponification Value	Acetyl Value by			
			Distillation Process	Filtration Process		
		I	II	III		C C
1	Castor oil,	I 311.2	150.5	149.6	..	.
	" "	II 310.3	149.9	149.4	..	0.0
	" "	III 312.1		146.7	..	0.1
2	Cottonseed oil,	I 213.3	24.76	25.1	..	
	" "	II 216.5	..	21.1	..	
	" "	III 214.7		21.9	..	
3	Maize oil,	I 201.5	8.75	8.25	..	0.0
	" "	II 200.9	7.81	8.21	..	..
	" "	III 192.9	17.2	16.6	7.62	0.0
4	Colza oil,	I 203.1	12.78	13.48	13.48	.
5	Olive oil,	II 204.7		13.62	13.44	..
6	Linseed oil,	I 208.5	6.85	6.92	6.92	..
	" "	II 210	7.03			..
7	Shark liver oil,			17.83	..	..
8	Animal oil,	221	22.04	23.38	..	..
9	Horse's foot oil,	214		14.40	..	..
10	Tallow S. America),	202.4	9.52	9.82	..	..
11	Beef-marrow,	203.6	6.63	6.64	..	..
12	Croton oil,	I 236	40.68	41.09	..	..
	" "	II 237.1	40.85	40.91	..	..
	" "	III 240.4	..	53.55	..	..
13	Coconut oil,	..	57.29		..	..
14	Butter-fat,	..	45.23		..	..

### Oxidation of Oils—Drying Properties.

Many of the fixed oils thicken on exposure to air, and, under favorable circumstances, gradually dry up into yellowish, transparent varnishes or resins. The oils which possess this property are termed drying oils, and contain *linolin* or its homologues.

For testing drying properties, a definite number of drops of the sample may be placed in a watch glass or flat porcelain capsule, and exposed to a temperature of about 100° C for twelve or twenty-four hours, side by side with samples of oil of known purity. Olive oil will be scarcely affected by such treatment, and rape oil will only thicken somewhat. Cottonseed oil will be considerably affected, while good linseed oil will form a hard skin or varnish, which can only with diffi-

<sup>1</sup> Should be accepted with reserve.



culty be ruptured by pressure with the finger. In some respects, a preferable plan is to flood a slip of glass with the oil to be tested, in the manner in which a glass-plate is covered with collodion. The glass with the adhering film of oil is then kept at  $100^{\circ}$ , and the progress of the drying watched by touching, at intervals, successive parts of the plate with the finger. Another useful method is to soak a definite measure of thick filter paper in the sample of oil, and then expose it to  $100^{\circ}$  or  $130^{\circ}$  C for some hours, side by side, with samples of oil of known purity.

Livache has shown that the rate of absorption of oxygen is accelerated by the addition of finely divided lead. The following description of the method of applying this principle to the examination of oils is taken from Lewkowitch ("Chem. Anal. of Oils, Fats, Waxes")

The lead-powder is prepared by precipitating a lead salt with zinc, washing the precipitate rapidly in succession with water, alcohol, and ether, and finally drying in a vacuum.

The method of operation is as follows—Spread about 1 gm. of the lead, weighed off accurately, on a somewhat large watch-glass in a thin layer, and then allow to fall on to it from a pipette 0.6 to 0.7 gm. (not more) of the oil to be tested, placing each drop on a different portion of the lead, and taking care that the drops do not run on to one another. Then allow the watch-glass to stand at the ordinary temperature in a place exposed to light.

Drying oils will be found to have absorbed the maximum quantity of oxygen after eighteen hours, or in some cases after three days, whereas non-drying oils do not gain weight until the fourth or fifth day.

The free fatty acids, with the notable exception of cottonseed oil acids, behave like the oils, i. e., their increase in weight corresponds to the gain in weight of the corresponding neutral oils. Livache's results are as follows—

	GAIN IN WEIGHT OF 100 PARTS		
	Of Oil After		Of Fatty Acids After
	Two Days	Seven Days	Eight Days
Linseed oil, . . . .	14.3		11.0
Walnut oil, . . . .	7.9		6.0
Poppyseed oil, . . .	6.8	.	3.7
Cottonseed oil, . . .	5.9	.	0.8
Beechnut oil, . . .	4.3		2.6
Colza oil, . . . .	0.0	2.9	2.6
Rape oil, . . . .	0.0	2.9	0.9
Sesame oil, . . . .	0.0	2.4	2.0
Arachis oil, . . . .	0.0	0.8	1.3
Olive oil, . . . .	0.0	1.7	0.7

To obtain a correct estimation as to the drying properties of an oil, regard

must be had not only to the increment in weight, but also to the length of time required. Thus, of the two oils in the following table, No. 1 must be considered the better, although both finally reach the same absorption of oxygen —

No. of Oil	Weight of Oil	Weight of Lead	Gain in Weight of 100 Parts After			
			One Day	Three Days	Six Days	Nine Days
1	3.246	1.012	14.4	15.7	unchanged	
2	3.154	0.653	2.45	12.0	15.9	unchanged

Bishop (*Abst. Analyst*, 105, 1896) calls attention to the fact that Lavache's process is serviceable only in the case of linseed oil, in other oils the oxidation proceeds too slowly. In order to obtain the most rapid oxidation the main essential is to have the oil as finely divided as possible, and for this purpose precipitated silica is employed. The oxidation is further hastened by the addition of manganese resinate. The commercial resinate is purified by treatment with ether or petroleum spirit, filtering, and evaporating the ether. The dry residue is powdered and kept in a stoppered bottle.

The method of determining the oxygen absorption is as follows. From 5 to 10 gram of the oil are weighed into a dish, and for 100 parts of the oil exactly 2 parts of the resinate added, that is, for 10 gram 0.2 gram. The mixture is agitated on the water bath until the resinate has dissolved and then allowed to cool. One gram of silica is weighed into a flat dish provided with a glass stirring rod, and then, drop by drop, by means of a pipette, 1.02 gram of the resinated oil added. The mass is intimately mixed and spread over the bottom of the dish, and is left at a temperature of from 17° to 25° C. for drying oils and of 20° to 30° C. for other oils. The dish is weighed after six hours and twice again in twenty-four hours, and so on until the maximum is attained, the mass being stirred after each weighing. The maximum increase in weight, multiplied by 100, gives the degree of oxidation. The following is a summary of the results —

Oils	Sp. Gr.	Degree of Oxidation	Mean Degree
Linseed, native, . . .	0.9327	17.70-16.40	17.05
"    in Plata, . . .	0.9304	15.45-15	15.20
Hempseed, . . .	0.9287	14.55-14.30	14.40
Poppy, native, . . .	0	11.50-13.90	14.20
Nut, " . . .	0	13.70	13.70
Cottonseed with stearin, . . .	0	8.60	8.60
"    without stearin . . .	0	9.60-9.30	9.45
Sesame, Senegal, . . .	0	8.95-8.50	8.70
"    Indian, . . .	0	7.40	7.40
Earthnut, African, . . .	0	6.70	6.70
"    white, . . .	0	6.50	6.50
Colza, native, . . .	0	6.40 (?)	6.40 (?)
"    Indian, . . .	0	5.90-5.80 (?)	5.85 (?)
Olive, . . . . .	0	5.30 (?)	5.30 (?)

Gellatly has pointed out the close relationship which exists between the drying properties of oils and their tendency to inflame spontaneously when exposed to the air in a finely divided condition. He found that when a handful of cotton-waste is imbued with the oil to be tested, and placed somewhat loosely in a paper box in an air-bath kept at 80° C., the mass enters into active combustion after a time dependent on the nature of the oil used. Thus, with boiled linseed oil inflammation occurred in little more than an hour, while raw linseed oil required four hours, and rape oil nine or ten to reach the same stage. Equal parts of seal oil and mineral oil refused to ignite, and even 20 per cent. of mineral oil materially delayed the ignition. The facts noted by Gellatly are interesting, and some of them have been confirmed by Renouard (*Jour. Soc. Chem. Ind.*, i 184) and other observers, but the method has no claims to quantitative accuracy.

Other methods of testing the oxidisability or drying character of linseed oil are described in the section treating of that substance.

Although frequently grouped as "drying" and "non-drying" oils, there is no sharp distinction between the two classes. Omitting the oils from marine animals, some of which dry rapidly, the chief commercial oils possess drying properties in the order of the following list, the most rapidly oxidisable being placed first.—Linseed, cottonseed and fancy seed, rape, arachis, olive, animal oleins.

The tendency of the fixed oils to dry or oxidise is in the direct order of their capacity for absorbing bromine or iodine, and of the rise of temperature produced on mixing them with concentrated sulphuric acid.

**OXIDISED OIL. BLOWN OIL. BASE OIL.**—Of late years there have appeared in commerce certain articles known as "oxidised oils," "blown oils," or "base oils." These are produced by blowing a stream of air through a fatty oil,—rape, cottonseed, or linseed oil being usually chosen for the purpose. A certain initial temperature is necessary to start the reaction, but afterwards the heat produced by the oxidation is sufficient to maintain the temperature required. By proper regulation, products can be obtained which closely simulate castor oil, and equal that body both in density and viscosity. Methods of distinguishing blown oils from castor oil are given in the section treating of the latter product.

**Determination of the Refractive Power.**—Valuable indications as to the purity of fats and oils, especially butter fat, may occasionally be gained from the determination of the refractive index.

This may be done by means of Abbé's refractometer, observing the total reflection which a thin stratum of the liquid placed between prisms of a more highly refracting substance produces in transmitted light. The following description of the method of using the instrument is taken from the bulletin of the A. O. A. C. —

A piece of fine tissue paper, 3 cm. in length by 1.5 cm. in width, is placed on the lower of the two glass prisms of the apparatus. Two or three drops of the sample are placed upon the paper, and the upper prism carefully fixed in position, so as not to move the paper from its place. In charging the apparatus with the oil in this way it is placed in a horizontal position. After the paper disk holding the fat is secured by replacing the upper prism the apparatus is placed in its normal position and the index moved until the light directed through the apparatus by the mirror shows the field of vision divided into dark and light portions. The dispersion apparatus is now turned until the rainbow colors on the part between the dark and light field have disappeared. Before doing this, however, the telescope, the eye-piece of the apparatus, is so adjusted as to bring the cross-lines of the field of vision distinctly into focus. The index of the apparatus is now moved back and forth until the dark edges of the field of vision fall exactly in the intersection of the cross-lines. The refractive index of the fat under examination is then read directly upon the scale by means of a small magnifying glass. To check the accuracy of the first reading, the dispersion apparatus should be turned through an angle of  $180^\circ$  until the colors have again disappeared, and the scale of the instrument again read. These two readings should nearly coincide, and their mean is the true reading.

For butter-fats the apparatus should be kept in a warm place, the temperature of which does not fall below  $30^\circ$ . For reducing the results to a standard temperature, say  $25^\circ$ , deduct 0.000176 for every degree above that point, since as the temperature rises the refractive index falls. The instrument used should be set with distilled water at  $25^\circ$ , the theoretical refractive index of water at that temperature being 1.3330.

The *oleo-refractometer* of Amagat and Jean (*Analyst*, 1890, 87) is a more convenient and satisfactory instrument for the examination of fats and oils. The oil to be observed is introduced into a hollow prism, which is immersed in a vessel with parallel sides filled with a standard oil. If the refractive power of the sample is the same as that of the standard, no deviation of the ray of light traversing the apparatus will take place; but otherwise deviation will occur, which can be measured on a micrometer scale placed on the eye-piece. The angle of the prism, the neutral or standard oil, and the division of the scale are all arbitrary. The standard oil sold with the instrument is sheep's-foot oil.

The following table shows the differences observed by Jean and others when various oils were compared. The purification of the oils, when stated, was effected by shaking with alcohol to remove the free fatty acids.

	ACIDITY.	DEVIATION		REMARKS	OBSERVER.
		Commercial	Purified		
Olive oil, . . .	. .	0 to +2		20 samples	Jean
" " " "	"	+9	.	Very old	"
" " " "	"	+1 to +3.5	. .	105 samples,	Pearmain
				22° C	
Almond oil,	3.3	+6	+6		Jean
" " "		+5	+6		"
" "		+7	. .		Bruyn
					and
" "	. .	+8 to +10.5	. .	8 samples,	Van Leent
				22° C	Pearmain
Peach-kernel oil,	.	+7.5 - +11.5		2 samples,	Pearmain
				22° C	
Arachis oil, .	. .	+3.5	+3.5	Rufisque	Jean
" " "		+4.5	+4.5		"
" " "	4.4	+4	+4.5	Gambia	"
" " "	8.0	+5	+6.5	Boulon	"
" " " "	1.7	+3.5	+3.5	La Félicité	"
" " "	.	+5 to +7		5 samples,	Pearmain
				22° C	
Teanseed oil, . .	. .	+8	.	22° C	Pearmain
Rapeseed oil, .	.	+16 to +20	.	8 samples,	Pearmain
				22° C	
" " "	1.3	+18	+18		Jean
" " "	11.6	+16	+18.5		"
" " "	+4.6	+17.5	+18	India	"
			. .		"
Cottonseed oil, .	0.4	+20	. .	Pale	Jean
" " (crude)	0.3	+20	. .	Yellow	"
		+16 to +17		3 samples,	Pearmain
				22° C	
" " (refined)	. .	+17 to +23		6 samples,	"
				22° C	
Sesame oil, .	2	+18	. .		Jean
" " " "	4.1	+17.5	.	Bombay	"
" " " "	. .	+17	+17	Pale	"
" " " "	.	+45	. .	. .	Bruyn
					and
" " " "	. .	+13 to +17	. .	5 samples,	Van Leent
				22° C	Pearmain

	ACIDITY	DEVIATION		RE MARKS	OBSERVER
		Commercial	Purified		
Sunflower oil,	.	+ 35	.	22° C	Pearmain
Camelina oil,	. .	+ 32	. .		Jean
Beechnut oil,	. .	+ 16 5	. .	. .	Jean
Linseed oil,	+1 5	+ 53	+ 54		Jean
" "	2 6	+ 48	+ 48		"
" " . .	. .	+ 49 to + 51	. .	.	Bruyn and Van Leent
" (crude)	.	+ 48 to + 52	.	3 samples, 22° C	Pearmain
" (refined)	.	+ 50 to + 54	.	5 samples, 22° C	"
Hempseed oil,	13 8	+ 30	+ 32	.	Jean
" "	. .	+ 34	+ 32		"
" "	. .	+ 34 to + 37 5		4 samples, 22° C	Pearmain
Poppyseed oil, .	.	+ 29		.	Jean
" "	.	+ 23 5		.	"
" "	2 5	+ 25		.	"
" "	2 6	+ 35	+ 38	Very old	"
" "	3 7	+ 29 5	.		"
" "	.	+ 30 to + 35	. .	3 samples, 22° C	Pearmain
Nigerseed oil, .	. .	+ 26 to + 30	.	2 samples, 22° C	Pearmain
Walnut oil, .	. .		+ 35 to + 36	.	Jean
Castor oil, . .	6 3	+ 43	.	. .	
" " . .	1 4	+ 46	.	.	
" " . .	. .	+ 37	. .	Javan	Bruyn and Van Leent
" " .	. .	+ 40	.	Pharmaceu- tical	"
" " . .	. .	+ 41 to + 42 5	.	Indian	Deering and Redwood
" " . .	. .	+ 39 to + 42	.	8 samples, 22° C	Pearmain
Japanwood oil,		+ 75			Pearmain

FIXED OILS AND FATS.

	ACIDITY.	DEVIATION.		REMARKS	ON
		Commercial	Purified.		
Neatsfoot oil,		— 3 to — 4	.	.	Pe
" "		— 1 and — 3	.	2 samples, 22° C	
Lard oil, . . .		+ 5 5	.	.	Pe
" " . . . .		0 to — 1	.	6 samples, 22° C	
Tallow oil, . .	.	— 15	.	.	Pe
" " . . .	.	— 1 and — 5	.	2 samples, 22° C.	
Horse foot oil, .	.	— 6 to — 13			
Whale oil, . . .	.	+ 30 5		.	Pe
" " . . .		+ 42 and + 48	.	2 samples,	
Seal oil,	4 6	+ 15	+ 15 5	Pale	Pe
" " .	2 7	+ 8	+ 12 5	brown	
" " .		+ 30 and + 36	.	2 samples, 22° C	
Cod-liver oil,	28 6	+ 45	.	.	P
" "	11 2	+ 53	.	.	
" "	11 2	+ 38	+ 38	.	
" "	11	+ 50	.	.	
" "	.	+ 40 to + 46	.	8 samples, 22° C	
Shark liver oil,	.	+ 29 to + 35	.	3 samples, 22° C	P
Sperm oil, . .	5	— 17 5	— 17	.	
" "	3 3	— 12	.	.	
Bottlenose oil, .		+ 50	.		F
Butter-fat, .	.	— 25 to — 34	.	15 samples, 45° C	F
Margarine,		— 13 to — 18	.	7 samples, 45° C	I
Lard, . . .	.	— 8 to — 14	.	10 samples, 45° C	I
Tallow, . .		— 15 to — 18	.	6 samples, 45° C	I
Paraffin (soft),		+ 54 to + 58 5		2 samples, 45° C	I

Other forms of instruments used for refractometric examinations are Zeiss's butyro-refractometer, recommended by Wollny, and Pulfrich's refractometer. The latter, like Abbe's instrument, allows of a scientific determination of the refractive index.

### Temperature-Reactions of Oils.

The rise of temperature which ensues on treating a fixed oil with concentrated sulphuric or nitric acid, or bromine, is a measure of the extent and intensity of the chemical reaction which ensues. The use of sulphuric acid was originally proposed by Maumené (*Compt rend.*, xxxv, 572). The test has been investigated by Fehling, Faisst and Knauss, J. Muter, L. Archbutt, J. Baynes, and others, who have arrived at very different opinions as to its value. The discrepancies observed have been due largely to not working under exactly similar conditions. Among the sources of error is unnoticed variation in the strength of the acid. Maumené obtained so much greater rise of temperature by employing recently heated sulphuric acid that he supposed the existence of an isomeric variety of this body. The specific gravity of concentrated sulphuric acid was formerly regarded as evidence of its strength, but Lunge and Naef have shown that acids of 96 per cent. and of 99 per cent., and even of 95 per cent. and 100 per cent., have almost exactly the same density. Further, L. Archbutt has found that commercial concentrated sulphuric acid varies considerably in strength, the samples examined by him ranging from 92.7 to 97.4 per cent. of  $H_2SO_4$ , as ascertained by very careful titration with standard alkali. He gives the specific gravity of 97 per cent. acid as 1.8440 at 60° F (15.5° C).

L. Archbutt finds that if the acid employed be much weaker than 97 per cent. of  $H_2SO_4$ , the increase of temperature is notably less and the reaction inconveniently slow. On the other hand, the initial temperatures of the oil and acid do not affect the extent of the rise, but both should be at the same temperature, or an erroneous result will be obtained. The following method of performing Maumené's test is that recommended by Archbutt, and employed by the writer—50 grm. of the oil is weighed into a 200 c. c. beaker, and the latter immersed in a capacious vessel of water, together with the bottle of strong sulphuric acid, until they are both at the same temperature, which should not be far from 20° C. The beaker containing the oil is then wiped, and placed in a cotton-wool nest previously made for it in a cardboard drum, or a wider beaker. The immersed thermometer is then observed, and the temperature recorded. 10 c. c. of the concentrated sulphuric acid should then be withdrawn from the bottle with a pipette, and



allowed to run into the oil. During the addition of the acid, which should occupy about one minute, the mixture must be constantly stirred with the thermometer, and the agitation continued till no further rise of temperature ensues. This point is readily observed, as the indication remains constant for a minute or two, and the temperature then begins to fall.

The results obtained from a particular oil are remarkably constant when the acid is of a uniform strength, and a defined method of manipulation is rigidly adhered to, but apparently insignificant differences in the mode of operation result in serious discrepancies in the results. Thus, Archbutt observed a rise of  $78.5^{\circ}$  when the oil was stirred until all the acid was added, and the thermometer then held stationary in the middle of the oil, but when the stirring was continued until no further rise of temperature was observed, the increase was only  $73.5^{\circ}$ .<sup>1</sup>

The object sought to be attained by Maumené's test is a determination of the intensity of the chemical action between the oil and the acid when employed in the proportions prescribed. It is evident that there may readily be local overheating, and that the uppermost stratum of oil and the froth on the surface are likely to be at the highest temperature, but the information sought is the maximum temperature attained by the *whole mixture*, taking care to avoid loss as far as possible by surrounding the vessel with a non-conducting medium. These conditions are best attained by using a thin vessel, well surrounded with cotton-wool, mixing the oil and acid as completely as possible, and taking as the true determination the highest temperature indicated by the thermometer, and maintained for more than a few seconds, ignoring any abnormal temperature which may be momentarily reached, but which the rapid fall on more perfect mixing shows to have been due merely to local action.

A simple stirrer may be made with a piece of thin tin-plate, fast-

<sup>1</sup> The effect of stirring has also been observed by J. Baynes, who, in a communication to the author, recommends that the experiment should always be commenced at  $20^{\circ}\text{C}$ , that the acid should have a density of 1.845, and that the mixture be effected in a cylinder  $1\frac{1}{2}$  inch wide, tightly packed in fibrous asbestos, instead of in a beaker in a nest of cotton-wool. He adds the acid during one minute, stirring continuously, and for a further period of five seconds only. The bulb of the thermometer is then held as closely as possible to the top layer of the froth, for if lowered a considerable fall in the temperature will be observed. Should the mixture show a tendency to froth over, it may be kept down by stirring, but the thermometer should be observed before doing so.

J. Muter first brings the oil and acid to a temperature of  $28^{\circ}\text{C}$ , and operates in a wide tube of thin glass mounted on a foot. The acid is added to the oil at the rate of 1 c.c. per five seconds, and the stirring continued during the addition, and for thirty seconds after wards.

ened to the thermometer by passing the bulb of the latter through two longitudinal slits in the plate. By rotating the thermometer and attached paddle between the finger and thumb, the contents of the beaker can be well mixed.

Owing to the notable difference in the rise of temperature caused by comparatively slight variations in the mode of operating, many of the recorded figures obtained by Maumene's test have little value. Hence it is desirable to compare a sample with one or more oils of known purity under exactly similar conditions. The figures in the table show the kind of result to be *expected* from various oils, but they must not be relied on too rigidly.

	RISE OF TEMPERATURE WITH SULPHURIC ACID, °C				
	Maumene	Baynes	Dobb	Archbutt	Allen
Olive oil,	42	40	39-43	41-45	41-43
Almond oil,	52-54	35	.	.	.
Rape and Colza oils, .	57-59	60-92	54-80	55-84	51-80
Almonds oil,	67	.	.	47-60	.
Beechnut oil,	65	.	.	.	.
Sesame oil,	68	.	.	65	.
Cottonseed oil; crude,	.	84	61	70	67-69
Cottonseed oil, refined,	.	77	.	75-78	74-75
Poppyseed oil, . . .	74	.	.	80-88	.
Nigerseed oil, . . .	.	82	.	.	81
Hempseed oil, . . .	98	.	.	.	.
Walnut oil, . . . . .	101	.	.	.	.
Linseed oil, . . . . .	103	104-124	.	.	104-111
Coconut olein, . . .	.	.	.	.	26-27
Castor oil, . . . . .	47	.	.	46	65
Lard oil, . . . . .	.	.	.	.	41
Tallow oil, . . . . .	41-44	.	.	.	.
Nantsfoot oil, . . . .	.	.	.	43	.
Horsefoot oil, . . . .	51	.	.	.	.
Whale oil, northern, .	.	.	.	.	91
Whale oil, southern, .	.	.	85-86	92	.
Porpoise oil, . . . . .	.	.	.	.	50
Seal oil, . . . . .	.	.	.	.	92
African fish oil, . . .	.	.	156	.	.
Shark-liver oil, . . . .	.	.	.	.	90
Codliver oil, . . . . .	102-103	116	.	.	113
Skate liver oil, . . . .	102	.	.	.	.
Menhaden oil, . . . . .	.	.	.	123-128	128
Sperm oil, . . . . .	.	.	.	51	45-47
Bottlenose oil, . . . .	.	.	.	42	41-47
Oleic acid, . . . . .	.	.	.	37½	38½

From these figures it will be seen that with some mixtures, for instance, olive with cottonseed oil and rape with linseed oil, the rise of temperature with sulphuric acid may afford a means of forming an approximate estimate of the proportion of ingredients. Thus, if the mean rise of temperature with rape oil be taken at  $58^{\circ}$ , and that of linseed oil at  $110^{\circ}$  C., a sample giving a rise of  $90^{\circ}$ , and known to consist of a mixture of the two, may reasonably be asserted to contain approximately 38.5 of rape and 61.5 of linseed oil.<sup>1</sup>

In the case of linseed and some fish oils, the reaction with sulphuric acid is violent. Dilution of the sample with an equal weight of olive or lard oil is advisable.

A valuable improvement in the mode of expressing the results of Maumené's temperature-reaction has been made by Thomson and Ballantyne (*J S C I*, 1891, 233). It consists in ascertaining the rise of temperature produced by mixing 50 grm. of water with 10 c.c. of strong sulphuric acid in the same vessel and under precisely the same conditions as those used for testing the oil. The *specific temperature-reaction* of the oil is obtained by multiplying the rise of temperature of the oil-acid mixture by 100, and dividing by the rise of temperature of the water-acid mixture.

The method possesses the great advantage that almost identical results are obtained with acids of somewhat different strengths (provided they are at least 95 per cent.), and hence the figures are much sharper and more distinctive. The following are the specific temperature-reactions for various oils as observed by Thomson and Ballantyne—

OIL	TEMPERATURE (WATER = 100)	NO. OF SAMPLES
Olive, .	89 to 95	11
Afuchs, .	105 to 137	2
Rape, .	125 to 144	5
Cottonseed, .	163 to 170	3
Linseed, . .	270 to 340	4
Castor, .	89 to 92	2
Whale, .	157	1
Seal, .	212 to 229	4
Codliver, .	243 to 272	3
Menhaden, .	306	1
Sperm, .	93 to 100	2

<sup>1</sup>  $110 - 58 = 52$ , or  $0.52^{\circ}$  C. (or about  $\frac{1}{2}$  degree) in excess of  $58^{\circ}$  for every 1 per cent of linseed oil present in the mixture. Hence the sample in question would contain  $90 - 58 = 32$ , and  $\frac{32}{52} \times 100 = 61.5$  per cent., or, more roughly,  $32 \times 2 = 64$  per cent.

**Bromine Thermal Value**—Hohner and Mitchell (*Analyst*, 1895, 147) have shown that the heat evolved in the reaction of bromine with unsaturated fatty bodies furnishes more definite data than is the case with sulphuric acid. As the action of bromine upon some oils is violent, it is moderated by the use of a diluent, such as chloroform or glacial acetic acid. The latter has the advantage, owing to its higher boiling point, of allowing a wider range of rise of temperature.

The procedure is as follows —

The bromine, oil, and diluent are all brought to the same temperature. One gram of the oil is placed in a Dewar vacuum jacketed test tube and dissolved in 10 c.c. of chloroform. Exactly 1 c.c. of bromine (measured by means of a pipette connected at the upper end with a narrow tube filled with caustic lime and having an asbestos plug at each end) is added and the rise in temperature measured by means of a correct thermometer divided into fifths. Fatty acids are dissolved in glacial acetic acid instead of chloroform.

Hohner and Mitchell have further shown that a definite relation exists between the rise of temperature thus obtained and the iodine absorption. In the particular vacuum tube and mode of operation employed by them, the factor was found to be 5.5. Each operator should ascertain for himself the factor applying to the individual case by determining the bromine thermal value of a non-drying oil, the Hübl number of which is known.

Although considerable differences are shown in the case of linseed and rape oil, Hohner and Mitchell consider that the determination of the iodine number by Hübl's method may be replaced by that of the bromine thermal value. In the case of the samples of linseed and rape oil it will be noticed that the calculated iodine number does not approximate closely the number obtained in the usual way. They offer the following explanation of these discrepancies — "Since linolic acid appears for each molecule of added bromine to evolve as much heat as does oleic acid, as shown by the figures given by cottonseed and almond oil respectively, it is probable that the same holds good for linoleic acid. The difference observed in the case of linseed oil might, on this assumption, be due to one or both of two causes. Either the Hübl number does not fully measure, in the case of highly drying oils, the unsaturated valency of the molecule, or the samples of linseed oil tested had undergone more or less oxidation, the oxygen or hydrogen group being replaced by the bromine."

As to the former alternative, it is well known that with highly-drying oils, after three hours' action of the Hübl solution, even in considerable excess, the maximum of absorption has by no means been reached, and the Hübl number is therefore almost certainly too small in these cases. As to the latter alternative, it has been shown by Ballantyne (*J. C. S. I.*, 1891, 32) that oils, after having undergone oxidation by exposure to air, show a higher Maumene figure than before. We are inclined to think that our calculated number expresses more accurately the real iodine combining capacity than does the Hübl figure in these cases.

"The two samples of rape oil examined by us do not show any agreement between the observed and calculated iodine number. We believe the samples to be pure, but the Hübl numbers—viz., 88 and 77—are materially lower than the numbers usually accepted for genuine rape oil. The calculated numbers, on the

other hand, obtained by multiplying the rise in temperature by 5.5, agree very well with the normal numbers of genuine rape oil. It appears very probable, therefore, that the samples of rape oil examined had undergone a considerable amount of oxidation, which lowered the Hubl number, but did not affect the bromine absorption, that, in fact, the figure calculated from the heat evolution in this, as in the case of linseed oil, is the correct iodine-absorption number."

COMPARISON OF OBSERVED AND CALCULATED RESULTS OF BROMINE THERMAL TEST.

OIL OR FAT	RISE IN TEMPERATURE WITH BROMINE	HUBL FIGURE	CALCULATED IODINE NO
Lard,	10.6	57.15	58.3
"	10.4	57.13	57.2
"	11.2	61.11	61.6
"	11.2	61.49	61.6
"	11.8	61.69	64.9
"	11.8	63.96	64.9
"	10.2	57.15	56.1
"	10.4	57.8	57.2
"	9.0	50.38	49.5
"	11.0	58.84	60.5
Lard, 10% cottonseed oil,	11.6	64.13	63.8
Lard, fatty acids,	10.4	59.6	57.2
"	11.0	59.15	60.5
Mutton tallow (kidney),	8.1	44.48	44.5
" (flax),	7.6	39.7	41.8
Butter,	6.6	37.07	36.3
"	7.0	38.60	38.5
" (fatty acids),	6.2	36.5	34.1
Almond oil,	17.6	96.64	96.68
Olive oil,	15.0	80.76	82.5
Maize oil,	21.5	122	118.2
Cottonseed oil,	19.4	107.13	106.7
Castor oil,	15.0	83.77	82.5
Linseed oil,	30.4	160.7	167.2
"	31.3	164.9	172
Rape oil,	18.4	88.33	101.2
"	17.6	77.2	96.8
Cod liver oil,	28.0	144.03	140
Oil sent as olive oil,	19.0	108.5	104.5
" " " "	19.2	105.7	105.6
" " " "	18.9	105.7	103.9

### Elaidin-Reaction.

When oleic acid is treated with a few bubbles of nitrogen trioxide, it is gradually changed into the isomeric body elaidic acid, which is solid at ordinary temperatures. Olein undergoes a similar change with production of the solid isomer elaidin, as also do such oils as consist of olein in a state of approximate purity. On the contrary, the drying oils, which consist chiefly of linolin and its homologues, are

not visibly affected by treatment with nitrous acid. Oils, which probably consist of mixtures of olein with more or less linolin, give less solid products with nitrous acid than the approximately pure oleins.

The effect can be produced by the gas evolved on heating starch or arsenous oxide with nitric acid; by a mixture of a nitrite with a dilute acid, by dissolving copper or mercury in nitric acid under a layer of the oil; by agitating the oil with a freshly prepared solution of mercurous nitrate, by the direct use of nitric acid of yellow or reddish color, and therefore containing lower oxides of nitrogen, and, lastly, by heating the oil with nitric acid until chemical action sets in and gaseous oxides of nitrogen are evolved. The proportion of the isomerising reagent requisite to produce the change and the influence of the proportion used on the rapidity and completeness of the reaction are almost unknown, and indeed no really scientific study of the formation of elaidic acid or elaidin appears to have been attempted.

The following method of obtaining the elaidin reaction, due to Poutet, has been studied by Archbutt, and is one of the best. It depends on the power of a solution of mercurous nitrate to retain nitrous acid.

One c.c. of mercury should be dissolved in 12 c.c. of cold nitric acid of 1.42 specific gravity. 2 c.c. of the freshly-made *deep green* solution is then shaken in a wide-mouthed stoppered bottle with 50 c.c. of the oil to be tested, and the agitation repeated every ten minutes during two hours. When treated in this manner, oils consisting of approximately pure olein, or of mixtures of olein with the solid esters, such as palmitin and stearin, give a solid product of greater or less consistency. Olive oil is remarkable for the canary or lemon yellow color and great firmness of the elaidin yielded by it. After twenty-four hours, the hardness of the product is such that it is impervious to a glass rod, and sometimes rings when struck with it, but this character is also possessed by the elaidins yielded by arachis and lard oils. In making the elaidin test, it is important to note the *time* required to obtain a "solid" product, which will not move on shaking the bottle, as well as its ultimate consistency. Also the temperature should be kept as nearly as possible constant, or erratic results may be obtained and comparison of different oils becomes impossible.

The behavior of the more important liquid fixed oils, when tested in the foregoing manner, is as follows:—

A *hard mass* is yielded by olive, almond, lard, sperm, and sometimes neatfoot and arachis oils.

*A product of the consistence of butter* is given by neat-foot, bottle-nose, mu-tard, and sometimes by arachis, sperm, and rape oils

*A pasty or buttery mass which separates from a fluid portion* is yielded by rape (mustard), sesame, cottonseed, sunflower, nigerseed, cod liver, seal, whale, and porpoise oils

*Liquid products* are yielded by linseed, hempseed, walnut, and other drying oils

L Archbutt has published the results of some experiments with a reagent, which is easily prepared and appears to possess certain advantages. It is made by passing a stream of sulphur dioxide into nitric acid (specific gravity 1.420) kept cold. When substituted for the mercurous nitrate, Archbutt's reagent yields, after a time, solid products with rape and cottonseed oils, in addition to the oils ordinarily giving solid elaidins. The cottonseed and rape oil products are at first red, and that from olive oil a bright green, but these tints soon fade.

In practice, the elaidin test receives its most important application in the assay of olive oil, with which it gives a very characteristic reaction. The subject is further discussed in the sections treating of olive and rape oils.

**REACTION OF OILS WITH SULPHUR CHLORIDE**—The vegetable drying oils are converted, on treatment with sulphur chloride ( $S_2Cl_2$ ), into gelatinous or elastic masses, which are employed as substitutes for india-rubber. T. P. Bruce Warren has investigated the reaction with a view to its employment in the analysis of oils. The effect of the treatment with sulphur chloride appears to vary materially with the proportion of the reagent used, which is usually 1 c.c., mixed with 1 c.c. of carbon disulphide, to 5 grm. of the sample, to which 2 c.c. of carbon disulphide has been previously added. The mixture is heated on the water-bath to constant weight, when the mass is broken up as completely as possible and exhausted with carbon disulphide, the solution obtained being evaporated to dryness and the residue weighed. The various fixed oils are said to give constant and characteristic weights of the original dry product, of which definite amounts are dissolved by subsequent treatment with carbon disulphide; but, in a few cases, these figures have not been published, and it does not appear that a mixture of two oils behaves in a manner which can be predicated from the nature of its constituents. Lard and other animal oils, including fish oils, are stated not to yield solid products with sulphur chloride, and the same is the case with coconut oil and the free fatty acids from any source. Blown or oxidised oils give black products

Warren claims the method is available for the determination of vegetable oils in butter and lard, of lard and cottonseed oils in olive oil, &c. For further details see *Chem. News* (56) 222, 231, 243, (57) 26, 43, 113; (58) 4, 15; (62) 27, 51, 125, 215, 251).

### Color-Reactions of Oils.

Many fatty oils give, when treated with chemical reagents, products which are often strongly colored. To a certain extent these color-reactions are characteristic of the oils by which they are produced, and hence may be employed for their identification. It must be borne in mind, however, that the albuminous, resinous, and other foreign matters, on the presence of which the color-reactions in most cases depend, are more or less completely removed or modified by the process employed for refining the oil. Hence, considerable variation is observed in the behavior of different samples of oil with the same reagent, and the value of the reactions is still further reduced by the modifications produced by the presence of free fatty acids in the oils. Still less are the indications to be trusted when mixed oils are examined. Notwithstanding these drawbacks, color-tests, when carefully applied, are often capable of furnishing valuable information, and sometimes render the positive identification of an oil, or its detection in a mixture, possible, when no other means are available.

Color-tests for oils have been devised by Calvert and various other observers, the most complete series of observations being those of Chateau, published in 1861.<sup>1</sup> Many of those proposed have very little value. Certain of them are useful as special tests, and are described in the sections treating of the oils for the detection of which they are of use. The reactions with strong sulphuric and nitric acid have a more general value, and require a fuller description. In employing color-tests for oils, it is very desirable to examine specimens of oils of known purity side by side with the sample, instead of trusting too implicitly to the reactions described.

**SULPHURIC ACID COLOR-TEST.**—Of color-tests, that with concentrated sulphuric acid is one of the most valuable and readily applied. It has been recommended by various chemists, some of whom employ several different strengths of acid, whilst others modify the proportion, that used by Chateau being in excess of the amount desirable. With care, the violet color produced by the fish liver oils is highly characteristic, as are also some of the other reactions.

<sup>1</sup> Chateau's tests, with some modifications by J. Mater, are described in Spon's *Encyclopædia of the Industrial Arts, &c.*, p. 1472 et seq.



The following table shows the effect produced on placing a drop or two of sulphuric acid in the centre of about twenty drops of the oil, and observing the color both before and after stirring. The reactions described include those produced by the majority of hydrocarbon oils. As already stated, the colors produced by different samples of the same kind of oil are liable to considerable variation.

The reactions of the oils with concentrated sulphuric acid are in some cases complicated or rendered indistinct by the charring action exerted by the reagent. This may be avoided by dissolving one drop of the oil in twenty drops of carbon disulphide, and agitating the solution with a drop of strong sulphuric acid. Whale oil when thus treated gives a fine violet coloration, quickly changing to brown, whereas with sulphuric acid alone a mere red or reddish-brown color changing to brown or black is obtained.

OIL	1 OR 2 DROPS OF STRONG SULPHURIC ACID TO 20 OF THE OIL	
	Before Stirring	After Stirring
<i>Vegetable Oils—</i>		
Olive oil, . . . . .	Yellow green, or pale brown	Light brown, or olive green
Almond oil, . . . . .	Colorless, or yellow	Dark yellow, olive, or brown
Arachis oil, . . . . .	Greenish-yellow to orange	Greenish, or reddish-brown
Rape oil, crude, . . . . .	Green, with brown rings	Bright green, turning brownish
Rape oil, refined, . . . . .	Yellow, with red or brown rings	Brown
Mustard oil, . . . . .	Dark yellow, with orange streaks	Reddish-brown
Cottonseed oil, crude, . . . . .	Very bright red	Dark red, nearly black
Cottonseed oil, refined, . . . . .	Reddish-brown	Dark reddish-brown
Sugarcane oil, . . . . .	Yellow, with brown clot	Reddish or greenish brown
Poppyseed oil, . . . . .	Yellow spot, with orange streaks or rings	Olive or reddish-brown
Linseed oil, raw, . . . . .	Hard brown or greenish-brown clot	Mottled, dark brown
Linseed oil, boiled, . . . . .	Hard brown clot	Mottled, dark brown
Castor oil, . . . . .	Yellow to pale brown	Nearly colorless, or pale brown.
<i>Animal Oils—</i>		
Lard oil, . . . . .	Greenish yellow, or brownish, with brown streaks	Mottled or dirty brown
Tallow oil, . . . . .	Yellow spot, with pink streaks	Orange red
Whale oil, . . . . .	Red, turning violet	Brownish-red, turning brown or black
Seal oil, . . . . .	Orange spot, with purple streaks	Bright red, changing to mottled brown.
Codliver oil, . . . . .	Dark red spot, with purple streaks	Purple, changing to dark brown
Sperm oil, . . . . .	Pure brown spot, with faint yellow ring	Purple, changing to reddish or dark brown
<i>Hydrocarbon Oils—</i>		
Petroleum lubricating oil, . . . . .	Brown	Dark brown, with blue fluorescence
Shale lubricating oil, . . . . .	Dark reddish-brown	Reddish-brown, with blue fluorescence
Roasin oil, brown, . . . . .	Bright mahogany brown	Dark brown, with purple fluorescence
Roasin oil, pale, . . . . .	Mahogany brown	Red-brown, with purple fluorescence

**NITRIC ACID COLOR-TESTS.**—The color-reactions of oils with *nitric acid* are sometimes characteristic, especially in the case of seed oils (See also under Cottonseed Oil). The test is recommended to be applied in various ways, but perhaps those methods which combine observations of the color and the character of the elaidin are to be preferred. Thus, O. Bach agitates 5 c.c. of the sample with an equal measure of nitric acid of 1.30 sp. gr. After noting any coloration the mixture is immersed in boiling water for five minutes and the effect again observed. A more or less violent reaction often occurs on heating, even resulting in the case of cotton or sesame oils in the mixture being projected from the tube. Bach gives the following table of results.—

KIND OF OIL	AFTER AGITATION WITH NITRIC ACID	AFTER HEATING FOR 5 MINUTES	AFTER STANDING 12 TO 15 HOURS
Olive, . . .	Pale green	Orange-yellow	Solid
Arachis, . .	Pale rose	Brownish-yellow.	Solid
Rape, . . .	Pale rose	Orange-yellow	Solid
Sesame, . .	White.	Brownish-yellow	Liquid
Sunflower, .	Dirty white	Reddish-yellow.	Buttery.
Cottonseed, .	Yellowish-brown	Reddish brown.	Buttery.
Castor, . . .	Pale rose	Golden-yellow	Buttery

A similar test has been described by Massie, who agitates 10 grm of the oil with 5 c.c. of nitric acid (sp. gr. 1.40) and 1 grm. of mercury, and observes the color of the product after one hour, and also the time required for solidification. Thus.—

OIL	COLORATION	MINUTES FOR SOLID- IFICATION	OIL	COLORATION	MINUTES FOR SOLID- IFICATION
Olive, . . .	Pale yellowish- green	60	Rape, . . .	Orange	200
Hazelnut, .	White	60	Cottonseed,	Orange-red	100
Almond, . .	White	90	Sesame,	Yellowish-orange	180
Arachis, . .	Pale reddish	105	Beechnut,	Reddish-orange	360
Apricot . . .	Rose	103	Poppy, . .	Red	Fluid
			Camelina,	Reddish-orange	Fluid

A mixture of strong *sulphuric* and *nitric acids*, used in the proportion of one drop to ten of the oil, has been proposed by H. Meyer as a color-test for certain fish oils. The following reactions were obtained with this test —

OIL	Sp Gr of Sample	BEFORE STIRRING	AFTER STIRRING
Cod-liver, .	929 0	Violet, quickly becoming rose red	Rose-red, changing to light brown
Hake liver,	927 0	Dark violet, changing to dark brown	Brownish-violet, changing to light brown
Skate-liver, . .	932 7	Light violet, changing to brown	Brownish-violet, changing to brown
Shark-liver, . .	928 5	Light brown, with spots of red	Light brown, becoming darker.
Herring,	932 6	Brown	Darker brown
Sprat, . . . .	928 4	Light brown.	Unchanged
Seal,	921 5	Light brown.	Lemon-yellow, rapidly changing to emerald-green and bluish green
Whale,	930 1	Light brown	Darker

### Classification of Fats, Oils, and Waxes.

In studying the characters of fixed oils, and identifying oils of unknown nature, valuable assistance is obtained from a suitable arrangement of the oils in classes or groups. The classification here adopted is based on a joint consideration of the origin, physical characters, and chemical constitution of the oils. An attempt is likewise made to classify the oils so that each group contains some important commercial oil which is typical of the other members of the group. Thus, the oils included respectively in the rape oil, olive oil, and coconut oil groups present a more or less close resemblance to rape oil, olive oil, and coconut oil respectively.

The researches of Hazura and others have shown that notable differences exist between animal and vegetable oils, and on this account, among others, it is not found desirable in practice to place in the same group an oil of animal origin (*e.g.* lard oil) with others of vegetable production (*e.g.* almond and olive oils), although in its physical and chemical characters it may closely resemble them. Similarly, the oils from fish and marine mammals are advantageously arranged in a separate class from the oils of terrestrial animals. It is evident that the melting point of an oil is chiefly dependent on its chemical composition, oils of which palmitin and stearin are the leading constituents, being solid at ordinary temperatures, while in the liquid oils olein or linolen predominates. The specific gravity of the fixed oils is also closely dependent on their chemical constitution, and

this becomes more evident when the determination is made at a temperature at which all oils are liquid. Under these circumstances, the waxes are of the least specific gravity, then follow the molten fats, the non-drying oils, the drying oils, and, lastly, castor oil, which is the highest of all.

I. OLIVE OIL GROUP—*Vegetable Oleins*.—The oils of this group have a specific gravity ranging from 914 to 920, and hence are lighter than the oils of Groups III, IV, and V. Their viscosity is notably greater than that of the drying oils, but inferior to that of rape oil, and they do not lose their power of producing a greasy stain on paper, however long they may be exposed to the air. They are further characterized by forming very solid elaidins, and by their moderate saponification-equivalents and iodine absorptions.

II. RAPE OIL GROUP.—The oils of this class are all derived from the *Crucifera*. They are generally classed as non-drying, though less perfect in this respect than the members of Group I, from which they are further distinguished by the greater heat developed when treated with strong sulphuric acid, by their higher iodine-absorptions, by forming pasty elaidins, and, above all, by their high saponification-equivalents—a character which is due to the presence of esters of fatty acids of exceptionally high combining weight.

III. COTTONSEED OIL GROUP.—In specific gravity these range from 920 to 926, or, when unrefined, somewhat higher. In this character, as also in their elaidin reactions, iodine absorptions and the temperatures developed with sulphuric acid, the members of the cottonseed oil group stand intermediate between the vegetable non-drying oils, typified by olive oil (Group I), and the true drying oils of Group IV.

IV. LINSEED OIL GROUP—*Drying Oils*.—These range in specific gravity from 924 to 937, and hence are distinctly heavier than the oils of the previous groups, though lighter than those of Group V. They are not solidified by treatment with nitrous acid, evolve great heat with strong sulphuric acid, and combine with large proportions of bromine and iodine. On exposure to the air in thin layers they absorb oxygen and form varnishes, which are at first sticky, but afterwards plastic or even brittle. The viscosity of the drying oils is less than that of the oils of the preceding groups.

V. CASTOR OIL GROUP.—The oils of this group have little in common beyond their great viscosity and high specific gravity, which ranges from 937 to 985. Castor and croton oils are remarkable for their ready solubility in alcohol and glacial acetic acid, and their marked purgative properties.

VI PALM OIL GROUP.—These are solid vegetable fats, not containing notable quantities of esters of lower fatty acids. Their melting points are somewhat variable, and are capable of permanent alteration.

VII. COCONUT OIL GROUP.—The members of this group are solid vegetable fats, having high specific gravities and low saponification-equivalents. The members of the sub group A contain notable proportions of esters of lower fatty acids—that is, of acids distilling with greater or less facility at 100° C. in a current of steam. This character distinguishes them from nearly all other vegetable oils, and from all animal oils except butter-fat. The members of sub group B are wax-like bodies of peculiar constitution.

VIII. LARD OIL GROUP.—*Animal Oils*.—This group includes those natural and manufactured oils, fluid at ordinary temperatures, which are obtained from terrestrial animals. They resemble the marine animal oils by darkening under the action of chlorine, but are not turned brown by boiling with caustic alkalis. They do not dry appreciably on exposure to air, and give more or less solid elaidins with nitrous acid.

IX. TALLOW GROUP.—*Solid Animal Fats*.—This group comprises such fatty bodies from terrestrial animals as are solid or semi solid at ordinary temperatures. Butter-fat is distinguished from all other members of the group by its high specific gravity and lower saponification equivalent, due to the presence of a notable proportion of radiocles of butyric and other lower fatty acids.

X. WHALE OIL GROUP.—*Marine Animal Oils*.—This group comprises the majority of the fluid oils obtained from fish and marine mammals. They are distinguished as a class by their offensive fishy odor, which becomes more perceptible on warming; by the reddish-brown color they assume when subjected to the action of chlorine, and by the reddish or reddish-brown color produced on boiling them with a solution of caustic alkali. With concentrated sulphuric acid they give considerable rise of temperature and colorations, varying from light red to purple and brown. Most members of the group dry more or less on exposure to the air, and yield but little solid elaidin on treatment with nitrous acid. In these respects they resemble the vegetable oils of the cottonseed group, and have similar specific gravity. The oils from the sperm and bottlenose whales are peculiar, both as to their physical characters and chemical constitution, and form a separate class (Group XI). "Train oil" includes the oil from the blubber of any marine mammal.

**XI. SPERM OIL GROUP—*Liquid Waxes***—The members of this group differ from all the fatty oils of previous classes in consisting essentially of esters of the ethyl series. In this respect they resemble the true waxes, but are fluid at the ordinary temperature. They are of less specific gravity than the true oils both at the ordinary temperature and at the boiling point of water, and on saponification yield considerable proportions of solid higher homologues of ethyl alcohol. They do not dry or thicken notably on exposure to air and yield solid elaidins on treatment with nitrous acid.

**XII. SPERMACEI GROUP—*Waxes Proper***—The members of this group are solid at ordinary temperatures, and more or less resemble beeswax, the prototype of the class. They consist essentially of esters of the higher radicles of the ethyl series, with in some cases an admixture of higher monatomic alcohols and higher fatty acids in the free state. Carnauba wax seems also to contain diatomic alcohol-radicles. Sperm and bottlenose oils (Table XI) resemble the waxes in constitution, but are liquid at ordinary temperatures. The bodies known as Japan wax and myrtle wax (Table VII) are fats, not true waxes. Paraffin wax and mineral wax are hydrocarbons, and hence quite different in chemical constitution from the true waxes of animal and vegetable origin.

In the following tables the chief fats, oils and waxes of commercial or scientific interest are on the principles above described.—

# I.—OLIVE OIL GROUP

KIND OF OIL	SOURCE OF OIL	SPECIFIC GRAVITY AT 15° TO 15.3° C	SOLIDIFYING POINT °C	SAPONIFICATION INDEX	IODINE ABSORPTION	OTHER CHARACTERS, COMPOSITION, &c	CHIEF APPLICATIONS
Olive oil.	Fruit of <i>Olea Europaea</i>	914 to 917	+ 4 to - 6	203 to 205	79 to 83	Yellow to olive green, pleasant odor or earthy turn, rancid on standing. Contains stearin with traces of stearic and arachidin	Lubrication, greasing wood, for dyeing, for cooking, for soap-making.
Olive-kernel oil	Kernels of the olive ( <i>Olea Europaea</i> )	920		208	82	Extracted by C <sub>6</sub> or other solvents. Is greenish brown. Very soluble in alcohol, acids and alkalis. The pressed olive have resembles kernel oil, but is darker color, of unpleasant smell, and usually gives unsoluble aldin	
Almond oil	Nuts of <i>Amygdalus communis</i>	914 to 920	- 10 to - 20	227 to 294	93 to 101.9	Yellow and nearly colorless, mild, agreeable taste (compared to similar to olive oil)	Ornaments and candles.
Peach oil.	Kernels of <i>Prunus Persica</i>	918 to 920	Below 29	295 to 297	92.3 to 97.7	Closely resembles almond oil.	Substitute for almond oil
Apricot oil	Kernels of <i>P. Armeniaca</i>	918 to 920	Below 29	291	100 to 108	Closely resembles almond oil	Substitute for almond oil
Arachis oil, Earthnut oil.	Nuts of <i>Arachis hypogaea</i>	916 to 922	- 5	285 to 295	85.6 to 103	Free stearins have sp gr of oil the 1st of 290. Yellow or nearly colorless. Pleasant nutty flavor.	Substitute for oil, and adulterant of oil. Hard, non-stiff, and other oils. Nut-oil is a mixture of arachis and olive oils.
Teanseed oil.	Seeds of <i>Camelina sativa</i>	917 to 927	Very low	287	88	Closely resembles olive and almond oils. Forms firm elastin	

## II.—RAPE OIL GROUP.

Kind of Oil	Source of Oil	Specific Gravity		Solidifying Point °C	Saponifi- cation Equiva- lent	Iodine Ab- sorption	Other Characteristics, Composition, &c	Chief Applications
		15°-15.5° C	100° C					
Rapeseed oil, Colza oil.	<i>Brassica campe- stris</i> , <i>B. napus</i> and allied spe- cies.	911 to 917	883	-6 to -10	314 to 328	97 to 105	When unrefined, yellowish-brown or brownish-green, viscid liquid, with pe- netrating odor, becoming more pene- trating when heated. When refined, refined light yellow and nearly odor- less. Contains erucin and rapin with a little behenic. Gives a very imper- fect elastin.	Used for burning and lubricating; also for making olive oil - soap- making and greasing steel goods.
Cabbagseed oil	Seeds of <i>Brassic</i> <i>arvensis</i>	914		-12	320	-	Dark, disagreeable odor. Elastin like rape oil.	
Radishseed oil	Seeds of <i>Sinapis</i>	9175		-10 to -18	315	95 to 95	Reddish or brownish-yellow. Fatty elastin. In composition resembles rape oil.	As a substitute for rape oil.
Oil of black mus- tard	Seeds of <i>Sinapis</i> <i>arvensis</i>	916 to 920		-17 to -18	322	95 to 107		
Oil of white mus- tard	Seeds of <i>Sinapis</i> <i>alba</i>	9125 to 916		-8 to -16	327	92 to 98	Characters similar to oil of black mus- tard.	As a substitute for rape oil.
Hedge-mustard oil.	<i>Raphanus repa- nistrum</i>	9175		-8	322	105	Characteristic taste, first mild, then acrid. On heating, becomes black, sulfuring, and adding hydrochloric acid, gives grass-green color.	Substitute for rape oil.
Jamboo oil	A species of <i>Ba- sisia</i>	915 to 916		-10 to -12	226	95 to 96		Substitute for rape oil.



# III — COTTONSEED OIL GROUP.

KIND OF OIL	SOURCE OF OIL	SPECIFIC GRAVITY		SOLIDIFYING POINT °C	SAPONIFICATION EQUIVALENT	IODINE ABSORPTION	OTHER CHARACTERS, COMPOSITION, &c.	CHIEF APPLICATIONS
		15° to 15° C	85° to 100° C					
Cottonseed oil	<i>Gossypium barbadense</i> and allied species.	916 to 930	867 to 872	1 to 10	237 to 254, usually 252	102 to 111	When crude, ruby-red or reddish brown, and gives blue coloration when saponified with caustic soda. Becomes darker yellow on cooling. Deposits much stearin on cooling. Bland, agreeable taste.	Cooking, manufacturing margarine, compound lard, soap-making, adulterating other oils, in U. S. ointments.
Cress-seed oil	<i>Lepidium sativum</i> .	920 to 924	-	- 15	315		Brownish yellow. Taste acid and disagreeable. Moderately viscous. Light yellow becoming darker on keeping. Odorless, mild taste, dries slowly.	
Grapeseed oil	<i>Vitis vinifera</i> .	920 to 926	-	- 10 to - 17	314	94 to 96	Light yellow becoming darker on keeping. Odorless, mild taste, more viscous than olive oil. Contained in the seed, colorless, bland and agreeable taste.	Cookery, pharmacy, margarine, soap-making, adulterating almond and olive oils.
Maize oil	<i>Zea Mays</i> .	918 to 924	-	- 10 to - 20	290 to 298	111 to 122	Yellow, more viscous than olive oil. Contained in the seed, colorless, bland and agreeable taste.	Cookery, pharmacy, margarine, soap-making, adulterating almond and olive oils.
Sesame or tseol oil	Seeds of <i>Sesamum orientale</i> or <i>indicum</i> .	921 to 924	868	- 4 to - 6	292 to 299	103 to 112	Yellow. Consists chiefly of linolin with but little olein.	Wool-dressing, burning soap-making, adulterating olive oil.
Sunflower oil	Seeds of <i>Helianthus esculentus</i> , <i>H. praecox</i> .	924 to 926	-	- 15 to - 18.5	289 to 298	122 to 145	Light or amber yellow, viscous, mild, sweet taste, no marked odor. Consists chiefly of linolin, peculiar taste and smell, dries slowly.	Perfumery, in pharmacy as a substitute for cod liver oil. Burning, painting.
Hazelnut oil	<i>Corylus avellana</i> .	929 to 936	-	- 10 to - 19	285 to 293	83 to 89	Yellowish, peculiar taste and smell, dries slowly.	
Camelina oil	Seeds of <i>Myoporum sibiricum</i> .	929 to 933	-	- 18 to - 19	298	132.6 to 135.3	Clear yellow, odorless, tasteless or slightly acrid.	In France, for cooking, burning and soap-making.
Beechnut oil	<i>Fagus sylvatica</i> .	928 to 932	-	- 3 to - 17	291 to 294	104.4 to 111.2		

# IV.—LINSEED OIL GROUP.

KIND OF OIL	SOURCE OF OIL	SPECIFIC GRAVITY		SOLUBILITY IN ALCOHOL AT 10° C.	SAPONIFI- CATION EQUIVA- LENT	IODINE ABSORP- TION	OTHER CHARACTERS, COMPOSITION, &c	CHIEF APPLICATIONS
		15° to 15° C.	100° C.					
Linseed oil	<i>Linum usitatissimum</i> , <i>L. perenne</i>	931 to 937	887	-20 to -27	288 to 300	170 to 181	Contains chiefly linolenin and isolinolenin with some theo- lin and stearin	Paints, varnishes, soft- soap, oilcloth- ing, oil 18, adulterating Paints varnishes, soft- soap-making
Hempseed oil	<i>Cannabis sativa</i>	925 to 931		-15 to -20	280	143 to 160	Greenish yellow, becoming brown on keeping, disagree- able smell and insipid taste Often mixed with linseed oil	
Poppyseed oil	<i>Rapumet sativum</i>	924 to 927	-	-18	280	134 to 143	Straw yellow, limpid, odor- less, almond flavor (no narcotic properties) Much resembles olive oil Soluble in 25 parts of cold or 6 of boiling alcohol Dries rapidly	Culinary purposes, burning, painting, adulteration of olive oil.
Tobaccoseed oil	<i>Nicotiana glauca</i>	923		-25	"		Greenish yellow, odorless, slightly viscous, highly in- soluble in alcohol Dries rap- idly	
Wetseed oil	<i>Berda indica</i>	936		Below -15	"		Dark green, thin, viscid, odor and taste Dries rap- idly	
Nigerseed oil	<i>Gnaphalium oleiferum</i>	924 to 928	873	Below -9	288 to 295	133	Pale yellow, sweet, more bio- pid than rape oil Dries readily and completely at 100° C	Adulteration of rape oil, substitute for linseed oil
Walnut oil	<i>Juglans regia</i>	925 to 927	"	-15 to -28	286	132 to 151	Greenish or yellowish, becom- ing lighter on keeping, viscid, agreeable functional and bulky taste when fresh, afterwards acid Highly soluble in alcohol	Paints and varnishes
Scotch fished oil	<i>Pinus sylvestris</i>	931		-27 to -30	294	119 to 120	Brownish yellow Dries easily	

# V.—CASTOR OIL GROUP.

KIND OF OIL	SOURCE OF OIL	SPECIFIC GRAVITY		SOLUBILITY IN 100 P. C.	SAPONIFICATION NUMBER	IODINE NUMBER	OTHER CHARACTERISTICS, COMPOSITION, &c.	CHIEF APPLICATIONS.
		15° to 15° C.	100° C.					
Castor oil	Seeds of <i>Ricinus communis</i>	958 to 970	969	— 18	32 to 119	33 to 85	Very viscous. Contains ricinolein and small amounts of stearin, myristin, and palmitin. Soluble in 4 measures of cold rectified spirit, or in own measure of cold glacial acetic acid. Insoluble in water. Specific gravity increases with age. Taste at first mild, then strong and burning. Intensely purgative. Solubility in alcohol is variable. Easily oxidized and becomes rancid. Thickens when applied to the skin. Gives little or no solid residuum. Thickens somewhat on exposure to air. Contains small amounts of free fatty acids, laurin, myristin, palmitin, and stearin. $\text{H}_2\text{SO}_4$ turns oil red, dissolves, and black.	In medicine, making liniments, ointments, toilet soaps, lubricating heavy machinery, making tarkey-red oil in medicine.
Croton oil	Seeds of <i>Croton tiglium</i>	940 to 960	—	— 16	251 to 270	101 to 105	Very viscous. Contains ricinolein and small amounts of stearin, myristin, and palmitin. Soluble in 4 measures of cold rectified spirit, or in own measure of cold glacial acetic acid. Insoluble in water. Specific gravity increases with age. Taste at first mild, then strong and burning. Intensely purgative. Solubility in alcohol is variable. Easily oxidized and becomes rancid. Thickens when applied to the skin. Gives little or no solid residuum. Thickens somewhat on exposure to air. Contains small amounts of free fatty acids, laurin, myristin, palmitin, and stearin. $\text{H}_2\text{SO}_4$ turns oil red, dissolves, and black.	In medicine, making liniments, ointments, toilet soaps, lubricating heavy machinery, making tarkey-red oil in medicine.
Carmine oil	Seeds of <i>Croton purgans</i> or <i>Adiantum purgans</i> (purgative)	911 to 920	—	— 9 to — 8	240 to 270	101 to 127	Very viscous. Contains ricinolein and small amounts of stearin, myristin, and palmitin. Soluble in 4 measures of cold rectified spirit, or in own measure of cold glacial acetic acid. Insoluble in water. Specific gravity increases with age. Taste at first mild, then strong and burning. Intensely purgative. Solubility in alcohol is variable. Easily oxidized and becomes rancid. Thickens when applied to the skin. Gives little or no solid residuum. Thickens somewhat on exposure to air. Contains small amounts of free fatty acids, laurin, myristin, palmitin, and stearin. $\text{H}_2\text{SO}_4$ turns oil red, dissolves, and black.	Substitute for castor oil. Said to be added to olive oil.
Japanese or Chinese wood oil	Seeds of <i>Albizia coriaria</i> or <i>Zizyphora coriaria</i>	937 to 940	Below — 13	Below — 13	255 to 300	150 to 157	Very viscous. Contains ricinolein and small amounts of stearin, myristin, and palmitin. Soluble in 4 measures of cold rectified spirit, or in own measure of cold glacial acetic acid. Insoluble in water. Specific gravity increases with age. Taste at first mild, then strong and burning. Intensely purgative. Solubility in alcohol is variable. Easily oxidized and becomes rancid. Thickens when applied to the skin. Gives little or no solid residuum. Thickens somewhat on exposure to air. Contains small amounts of free fatty acids, laurin, myristin, palmitin, and stearin. $\text{H}_2\text{SO}_4$ turns oil red, dissolves, and black.	As a drying oil.
Boiled linseed oil	Made by heating linseed oil	939 to 950	—	298	—	—	Very viscous. Contains ricinolein and small amounts of stearin, myristin, and palmitin. Soluble in 4 measures of cold rectified spirit, or in own measure of cold glacial acetic acid. Insoluble in water. Specific gravity increases with age. Taste at first mild, then strong and burning. Intensely purgative. Solubility in alcohol is variable. Easily oxidized and becomes rancid. Thickens when applied to the skin. Gives little or no solid residuum. Thickens somewhat on exposure to air. Contains small amounts of free fatty acids, laurin, myristin, palmitin, and stearin. $\text{H}_2\text{SO}_4$ turns oil red, dissolves, and black.	Paints, varnishes, oil-cloth-making.
Blown oils.	Made by oxidation of rape, cotton, linseed, lard, and other oils.	942 to 955	—	275 to 294	—	—	Very viscous. Contains ricinolein and small amounts of stearin, myristin, and palmitin. Soluble in 4 measures of cold rectified spirit, or in own measure of cold glacial acetic acid. Insoluble in water. Specific gravity increases with age. Taste at first mild, then strong and burning. Intensely purgative. Solubility in alcohol is variable. Easily oxidized and becomes rancid. Thickens when applied to the skin. Gives little or no solid residuum. Thickens somewhat on exposure to air. Contains small amounts of free fatty acids, laurin, myristin, palmitin, and stearin. $\text{H}_2\text{SO}_4$ turns oil red, dissolves, and black.	Substitutes for castor oil for lubricating.

# VI—PALM OIL GROUP.

KIND OF FAT	SOURCE OF FAT.	SPECIFIC GRAVITY		MELTING POINT °C	SOLIDIFYING POINT °C	SATURATION EQUIVALENT	FODDER ABSORPTION	OTHER CHARACTER, COMPOSITION, &c	CHIEF APPLICATIONS
		15-10° C	98-99° C						
Palm oil	Fruit of <i>Adansonia digitata</i> or <i>Elaeis guineensis</i>	920-945	837-851	27 to 32.5	20 to 36	277-286	48-54	-	Railway grease soap and candle making
Cacao-butter	Nuts of <i>Theobroma cacao</i>	915-976	857-858	30 to 34	20.5	278-292	34-45	Colorless, chocolate-like taste and smell, not liable to become rancid	Pharmacy chocolate, "cocoa butter," high-class toilet soaps
Nutmeg-butter mace-butter	Nuts of <i>Myristicifera fragrans</i>	945-956	893	25 to 34	20 to 27	348-364	31-32	Reddish yellow or mottled taste and odor of nutmeg, firm consistence. Occurs in commerce in oblong cakes covered with leaves. Soluble in a few drops of hot alcohol. Contains a few per cent of volatile oil, free myristic acid and myristicin, and scum.	Pharmacy, high-class toilet soaps
Dika fat	Seeds of <i>Irvingia gabonensis</i>			29 to 42	34 to 35		31	Orange-yellow color, turning to yellowish gray on melting, characteristic odors	-
Barberry tallow Shea- or gaham-butter	Seeds of <i>Bassia Parlati</i> (tropical Africa)	9175	859	23 to 43	17 to 23	292-313	14 56 57	White, grey, greenish, or reddish, faint, characteristic, resinous odor and agreeable flavor. Somewhat resembles tallow	Soap-making
Mahwah-butter	Seeds of <i>Bassia latifolia</i> (tropical Africa)	9175		28 to 31	19 to 22	280-299	60-62	Greenish or yellowish	-
Bassia or allipe oil.	Seeds of <i>Bassia longifolia</i> (India) and allied species.	947		33 to 42	35	281	60	Greenish, rancid taste, consistency of butter	Soap-making when tallow and palm oil are scarce
Chinese tallow	Berries of <i>Silingia sebifera</i>	9175	864	35 to 44	24 to 35	278-315	39-45	Greenish or white, turns brown on exposure, faint odor	-
Cottonseed scum	From cottonseed oil	918-923		-36 to 40	16 to 32	285-294	89-104	Resembles tallow	Adulterating lard, margarine

# VII — COCONUT OIL GROUP

Kind of Fat	Source	SPECIFIC GRAVITY		MELTING POINT °C	SOLIDIFYING POINT °C	SAPONIFICATION NUMBER LAST	IODINE ABSORPTION	OTHER CHARACTERISTICS, COMPOSITION, &c.	Chief Application
		At 15° to 16° C	At 99° to 100° C						
Coconut oil	Nuts of <i>Cocos nucifera</i> and <i>C. borhyraea</i>		868-874	20 to 28	14 to 27	200 to 228	8 to 9.5	Consistency of butter White or slightly yellow and slightly translucent. Tastes of coconut. Contains esters of all acids known, but none of those forming even number of carbon atoms from acetic to arachidic. Chiefly laurin Myristic and capric acids present in small amounts.	Various soap, candle-making, artificial butter
Palmist or palm kernel oil.	Kernels of nut of <i>Attorea olea</i> or <i>Elettaria guineensis</i>	952	866-873	23 to 25	20 to 26	224 to 228	10.5-17.5	Consistency of coconut oil Translucent and in character composition. Usually pink or pinkish and has peculiar taste and odor.	Substitute for coconut oil
Laurel oil	Fruit of <i>Laurus nobilis</i>	944	876	2 to 26	24 to 25	233	40 to 80	Consistency of butter, green color, very viscous, and peculiar taste and odor. Contains esters of acetic, lauric, and myristic acids, with stearin, pinolen, and capric acids.	Veterinary and quack medicines
Macassar oil.	Seeds of <i>Sclitoclethra y g</i>	924		22 to 23		244 to 255	48 to 53	Butter-yellow oil per centage of acetic, butyric, lauric, arachidic, and stearic acids.	Candle-making
Japan wax.	Berries of <i>Platanus indica</i>	984 to 1,000 974 to 982	874-877	50 to 56	42 to 52	252 to 267	4.2 to 6.6	Hard, pale green	Candle-making
Myrtle wax.	Berries of <i>Myrica cerifera</i>	955	875	40 to 44	39 to 43	265 to 270	10.7 to 12.0 in benzene ref 6.34		

# VIII.—LARD OIL GROUP.

KIND OF OIL	SOURCE	SPECIFIC GRAVITY AT 15° TO 16° C	SMOKING POINT °C.	SAPONIFICATION EQUIVALENT	IODINE ABSORPTION,	OTHER CHARACTERS, COMPOSITION, &c.	CHIEF APPLICATIONS
Neatsfoot oil	The feet of various animals	914 to 916	Below 0	289 to 294	66 to 72	Yellowish, odorless, bland taste Not liable to become rancid. Often adulterated with bone oil, lard oil, and fish oils. Forms pasty clots in	Lubricating clocks and machinery exposed to low temperatures Leather dressing
Bone oil	Extracted from bones by boiling or solvent.	914 to 916	Variable	"	"	Yellowish to dark brown. Often contains calcium phosphate in notable quantity, which may be detected by the ash left on ignition, and separated by agitating the oil with dilute hydrochloric acid	Soap-making
Lard oil.	Obtained by pressing lard	915	-4 to + 10	286 to 296	67 to 82	Very slightly colored, clear, slight odor of lard. Soluble in an equal weight of boiling alcohol. Adulterated with earthen oil, &c	Lubricating, soap-making, adulterating olive oil, and wool-greasing, in America as a light-house oil
Tallow oil	Obtained by pressing tallow	916	0 to + 6	"	"	Viscid; much resembles lard oil crude oleic acid is often mis-called "tallow oil."	Soap-making, lubricating
Horsefoot oil.	Obtained by boiling horses' feet.	913 to 927	"	284 to 287	73 to 80		

# IX.—TALLOW GROUP.

KIND OF FAT	SOURCE	SPECIFIC GRAVITY AT 15° C.	MELTING POINT °C.	SOLIDIFYING POINT °C.	SAPONIFICATION INDEX	IODINE ABSORPTION	OTHER CHARACTERISTICS, COMPOSITION, &c.	CHIEF APPLICATIONS
Tallow, neat	From the ox and sheep	856 to 858	32 to 49	32 to 48	238 to 240	Back 36 to 45 Mutton 32 to 61	Melting-point varies much with part and nature of animal yielding the fat	Candles soap-making, lubricating.
Lard	From abdomen and back parts of the hog	859 to 860	28 to 45	27 to 44	262 to 262	46 to 63	Melting-point varies much with part of animal yielding the fat	Cooking, soap-making, etc.
Horse-fat	From the horse, &c.	861	.	..	285 to 287	74 to 86	Melting-point varies much with part of animal yielding the fat	Cooking, soap-making, etc.
Bone-fat	Bones of various animals.	888	.	..	294	..	Yellow or dirty white to brown, consistency of lard or harder, very variable in quality	Cooking, soap-making, etc.
Wool-fat (suint)	The wool of various kinds of sheep.	867 to 870	29 to 35	26 to 40	330	22 to 41	Brownish, unpleasant smell, usually softer than lard. Commonly contains large yellowish lumps. Contains a notable quantity of cholesterol. Take up much water.	Cheese "Brown Windsor" soaps
Butter-fat.	Cow's milk	859 to 863	34 to 49	18 to 38	255 to 270	46 to 61	Cloudy resembles butter of which it often contains a considerable proportion	Food Cooking
Margarine	Made from lard solid parts of animal fat with admixture of cotton-seed, or other oil, essences, or colorants.	863 to 868	54 to 65	..	285 to 291	63 to 85	Cloudy resembles lard.	Cooking
Compound lard	Hog's fat mixed with lard or tallow	863 to 868	54 to 65	..	285 to 291	63 to 85	The melting-point is high, closely resembles lard tallow or suet. Must not be confused with stearin and glycerine. Melting-point very variable, often contains wool-fat	Candles and night-lights, soap-making, etc.
Stearin	Obtained by pressing lard or tallow	863 to 868	54 to 65	..	285 to 291	63 to 85	The melting-point is high, closely resembles lard tallow or suet. Must not be confused with stearin and glycerine. Melting-point very variable, often contains wool-fat	Candles and night-lights, soap-making, etc.
Recovered fat, Yorkshire grease	Treatment of suet, &c., with acids	863 to 868	54 to 65	..	285 to 291	63 to 85	The melting-point is high, closely resembles lard tallow or suet. Must not be confused with stearin and glycerine. Melting-point very variable, often contains wool-fat	Candles and night-lights, soap-making, etc.

# X—WHALE OIL GROUP.

KIND OF OIL.	SOURCE	SPECIFIC GRAVITY AT 15° TO 16° C.	SAPONIFICATION EQUIVALENT	IODINE ABSORPTION	OTHER CHARACTERISTICS, COMPOSITION, &c.	CHIEF APPLICATIONS
Whale oil	Blubber of <i>Balaena mysticetus</i> and various allied species	920 to 931	250 to 296	110 to 127	Yellow or brown color, disagreeable fishy odor, ruinable by bleaching powder. Becomes alkaline when saponified. Some varieties dry rapidly. Sometimes contains valerin.	Illumination, soap-making.
Porpoise oil	Blubber of <i>Delphinus phocaena</i> and allied species	920 to 930	255 to 256	131	Yellow or brown. Much resembles whale oil. Contains valerin.	Illumination, soap-making, leather dressing, lubrication.
Seal oil	Blubber of <i>Phoca</i> of various species	916 to 929	288 to 301	125 to 152	Color ranges from brown to nearly water-white. Small disagreeable, but much improved by exposing the oil to air and light. Dries slowly.	Burning in safety-lamps, adulteration of cod-liver oil. Produces a very offensive-smelling soap.
Menhaden oil	<i>Alax menhaden</i>	927 to 933	292	143 to 160	Brownish color, fishy odor, dries readily. Sometimes adulterated with mineral oil.	Adulteration of linseed oil.
Cod-liver oil	Liver of various species of <i>Gadus</i>	922 to 930	263 to 323	126 to 166	Neerly colorless to brown. Disagreeable heavy taste. Contains cholesterol, and traces of iodine.	Medicine, leather-dressing.
Shark-liver oil	<i>Squalus maximus</i> (backing shark or sun-fish) and allied species.	911 to 923	286 to 400	90 to 114.6	Clear yellow color. Often enormously adulterated. Contains a notable proportion of cholesterol.	Leather-dressing, adulteration of cod-liver oil. (Not now in the market.)



# XI.—SPERM OIL GROUP.

KIND OF OIL.	SOURCE.	SPECIFIC GRAVITY		KHO PER SAPONIFICATION	SAPONIFICATION EQUIVALENT	IODINE ABSORPTION	OTHER CHARACTERISTICS, COMPOSITION, &c.	CHIEF APPLICATIONS
		At 15° to 16° C	At 98° to 100° C					
Sperm oil	Blubber and cranial cavities of <i>Physeter macrocephalus</i> .	875 to 884	822 to 830	12.3 to 14.7	380 to 454	81.3 to 85	Yellow, slightly unpleasant, fishy taste. Deposits crystals of spermaceti on cooling. Contains dodecetyl oleate or its homologues.	Lubrication of light machinery, hardening steel.
Dogging oil, or bottle-nose oil	Blubber, &c., of <i>Hyperoodon rostratus</i> and <i>H. lucius</i> .	876 to 881	823 to 828	12.3 to 13.4	419 to 456	80	Closely resembles sperm oil in character and composition. Said to contain dodecetyl diethylene.	Substitute for sperm oil.
Dolphin oil	Blubber, &c., of <i>Delphinus globiceps</i> .	922		15.7	284	99.5	Citron yellow, odor of once fishy and like that of leather. Soluble somewhat readily in alcohol. Deposits spermaceti when cooled, and contains a large proportion of the glyceride of stearic acid, besides monatomic ethers.	

# XII—SPERMACEI GROUP WAXES

KIND OF WAX	SOURCE	SPECIFIC GRAVITY		MELTING POINT °C	SOLIDIFYING POINT °C	PERCENTAGE OF KHO TOP SATURATION		CHEMICAL CONSTITUENTS			OTHER CHARACTERISTICS
		At 15° to 16° C	At 25° to 29° C			By Free Acid	Total	Free Acids	Alcohol	Ethers	
Sperm cet	Deposited from oil of the sperm whale and allied Cetacea	905 to 960	808 to 812	43 to 49	41 to 46	None or traces	12.8	None or traces		Cetyl palmitate and its homologues	White, highly crystalline when saponified, yields a palmitate and solid esters, alcohol, C <sub>18</sub> H <sub>36</sub> O <sub>2</sub> , and homologues extracted by ether from saponified liquid. Used in candles, and for candle-making.
Bee wax	The honey-comb of various species of bee	955 to 959, usually 962 to 966	819 to 829	62 to 64	60 to 62	2.0	9.3 to 9.6	Crotonic acid 12 to 15 per cent		M-cetyl palmitate and a little palmitic acid	Yellow, peculiar smell. When bleached, white. Wax leaves and fracture. Used for candle-making, moulding, etc. Adheres with milk, separates on heating, and other waxes.
Peel, India, or Chinese wax	Produced by a species of <i>Coccus</i> which punctures the twigs of certain trees		809 to 811	81 to 83	80 to 81	trace	6.3			Cetyl erucate and homologues	Semi-white, highly crystalline, brittle, exuded from its appearance, vegetable spermaceti. Often adulterated, frequently contains 15 to 20 per cent of other waxes.
Opium wax	Capsules of <i>Papaver somniferum</i>			79 to 82	76 to 80					Cetyl erucate and cetyl palmitate	White, crystalline. Soluble in boiling chloroform.
Palin wax	Bark of <i>Cratogeomys</i> of the Cordilleras of New Granada, the eastern slopes of the Cordilleras of South America	955 to 1.000	812	83 to 85	81 to 82	4 to 8	5.3 to 5.8	Crotonic acid 3 to 6 per cent, and a little of homologues	Myristic alcohol and a little cetyl alcohol	Myristic, erucate, and allied esters.	Much resembles carnauba wax.
Carnauba, Caranaba, or Brazil wax											Very hard, sulphur-yellow or yellowish-green. Not readily bleached without change. Used in candle-making, soap-making, and for indulating beeswax. Highly complex composition.

## EXAMINATION OF FATS AND CRUDE OILS FOR FOREIGN MATTERS.

By the term foreign matters used in this connection it is not intended to signify the traces of cholesterol, chlorophyll, gummy, albuminous, and coloring matters, which are *natural* constituents of the crude fats and oils, but the term is applied to large proportions of free fatty acids and admixtures of resin, soaps, hydrocarbons, water, and mineral matter. These bodies are often added, either as adulterants or with the view of conferring some special property. When in small quantity, the detection of some of them is attended with considerable difficulty.

In the case of butter, lard, and palm oil, more or less water, curd, and salt are not infrequently present. The methods of detecting and estimating such of these admixtures as are peculiar to each of these are described in the special sections. An oil, if clear, may be regarded as free from such extraneous matters, and their presence in a fat may usually be detected by melting the sample. If an opaque or opalescent oil result, or one containing visible particles of suspended matter or globules of water, it should be purified from these by filtration through dry paper before proceeding to search for resin, fatty acids, soap, or hydrocarbons.

Soap is sometimes directly added to an oil, but its presence is more frequently due to the use of alkali employed to increase density and viscosity. Soap is readily detected by dissolving the oil in about three times its measure of ether or freshly-distilled carbon disulphide, adding a little water, and agitating the whole thoroughly in a tamped separator. The soap will dissolve in the water, while the other foreign matters will dissolve with the oil, in the ether or carbon disulphide, and may be recovered therefrom by distillation. The soap may be determined by evaporating the aqueous liquid and weighing the residue after drying at 100° C. The proportion of soap may also be inferred from the amount of carbonate left after igniting the oil.

INSOLUBLE SOAPS are not infrequently present in oils, waste greases, and pharmaceutical preparations ("oleates"). Though insoluble in water, many of them are soluble in ether or petroleum spirit. They may be decomposed by agitating the mixture with dilute sulphuric acid, when the acid liquid will contain the metal of the soap, and a corresponding quantity of fatty acid will dissolve in the oily layer. When it is desired to ascertain the proportion of free fatty acids originally in the oil, a titration with alkali should be made both

before and after shaking with dilute acid. The difference between the two estimations represents the fatty acid produced by the treatment.

**Free Acid in Oils.**—Commercial oils and fats very frequently contain notable proportions of free acid, which may either be mineral acid, as a result of incomplete separation after refining, or free fatty acid resulting from unskilful refining or from the natural decomposition of the oil.

**MINERAL ACIDS** are only accidentally present in fixed oils, and usually exist in very small proportions. Even minute quantities are highly objectionable in oil intended for lubricating, but are harmless when the article is to be used for soap-making. Mineral acids may be readily recognized by agitating the oil with warm water, separating the aqueous liquid, and testing it with a solution of methyl-orange, which will give an orange or red coloration if any mineral acid be present. The nature of the mineral acid, which is most commonly sulphuric, can then be ascertained by testing the aqueous liquid with barium chloride, silver nitrate, and other appropriate reagents. Oils which, from over-treatment with acid during refining, contain a conjugated acid or sulphonate, must be boiled with water for some time, in order to decompose the compound.

**FREE FATTY ACIDS** are often normally present, and in some oils (e.g., olive and palm) may exist in very large proportion. Free oleic acid is largely used as a lubricant in wool-spinning, and free palmitic and stearic acids are employed for making candles and night-lights. All three acids are used for soap-making.

The fatty acids differ from neutral fats and oils in having an acid reaction in alcoholic solution; in being converted into soaps by treatment with alkaline carbonates or borax; and in being freely soluble in alcohol, even if the latter be somewhat dilute.

The free fatty acid may be detected by shaking the sample with alcohol, and adding an alcoholic solution of lead acetate to the spirituous liquid. If a notable quantity of free fatty acid be present, a white precipitate will result. Resin and soap produce the same reaction.

A more delicate method, which can be applied to the accurate *determination* of the quantity present, consists in titrating the alcoholic solution with standard caustic alkali, using phenolphthalein as an indicator. The method was first proposed by Hausmann, and test-analyses by Groger of artificial mixtures of known composition have fully established its accuracy. The following mode of operating is applicable to the determination of free fatty acids in whatever pro-

portion they may be present.—Some methylated spirit is purified by redistillation with a little caustic soda, a little alcoholic solution of phenolphthalein added, and then dilute caustic soda drop by drop till the liquid retains a faint pink color after shaking, this preliminary treatment being intended to secure the absence of any trace of free acid. An accurately weighed quantity of the sample, varying from 5 gm. of fatty acid to 50 gm. of an ordinary oil, are introduced into a flask or bottle furnished with a glass stopper, from 50 to 100 c c of the neutralised spirit is added and raised to the boiling point by immersing the bottle in hot water. The contents are thoroughly agitated to effect as complete a solution of the fatty acids as possible. If the sample of oil be wholly free from acid, the pink color of the spirit will remain unchanged, but otherwise it will have disappeared. In the latter case, a semi-normal solution of caustic soda is added in small amounts to the warm contents of the flask, agitating thoroughly after each addition until the pink coloration persists after vigorous shaking. The reaction is as well defined, and the neutralisation-point as easy to perceive, as in the titration of mineral acids, but owing to the very high combining weights of the fatty acids, great care is necessary.<sup>1</sup> Thus, 1 c c of semi-normal caustic alkali used corresponds to 0.126 of *palmitic*, 0.142 of *stearic*, or 0.141 gm. of *oleic acid*. For determining small proportions of free acid, it is desirable to employ decinormal alkali, while in the case of samples containing much free acid the quantity taken for the assay should be correspondingly reduced. In assaying palm oil, which often has a red color, the titration may be made on 5 gm. of the sample, dissolved in 20 c c of spirit, the flask being placed on a white surface.

*Resin acids* present in the sample will be estimated by the above process as fatty acids. Their separation from the latter is described below. *Mineral acids* will affect the accuracy of the results unless duly allowed for, or previously separated by repeatedly agitating the oil with water. *Soap* and *hydrocarbons* do not interfere.

The foregoing method may be supplemented by gravimetric determination. The resultant alcoholic liquid is separated from the oil, the alcohol evaporated, and water added. This solution is agitated with a little petroleum spirit (not ether) to dissolve suspended oil, the aqueous liquid separated, and the fatty acid liberated from the soap

<sup>1</sup> This method combines the advantages of the two methods of operating recommended by Archburt (*Analyst*, ix, 170) and W. H. Dering (*Jour. Soc. Chem. Ind.*, iii, 511), who have had considerable experience of the process. No practical difference is noted between the results obtained by titrating with aqueous alkali and with alcoholic alkali.

solution by adding dilute sulphuric acid. On agitating with ether, separating the ethereal solution, and evaporating it to dryness, the fatty acids can be weighed. This method should be used when resin acids may be present. In their absence, the determination should be fairly concordant with the result of the titration. *Soap* should be previously separated. *Mineral acids* and *hydrocarbons* do not interfere.

An areometrical method of estimating the proportion of free acid is described in the section on Olive Oil.

The detection of resin in fixed oils is attended with some difficulty, its determination is troublesome and occasionally impossible.

Common *rosin* or *colophony*, which is described in a special section, is added to oils to impart certain properties, but its employment often wholly unsuits them for their intended purposes.

One of the methods of detecting rosin is by the brown color it imparts to caustic soda. The original sample is saponified, the alcohol boiled off, and the liquid treated with sufficient caustic soda ley to cause precipitation of the soap. The solution, separated from the soap by decantation or filtration through glass-wool, will be dark brown if resin is present. The same reaction serves for the recognition of rosin in soap, previous saponification being unnecessary. The method may also be applied to the mixture of fatty and resin acids separated in the manner described in the table on page 117. The dissolved resin may be recovered by acidulating the alkaline liquid with hydrochloric acid, when a precipitate of resinous odor will be formed. The resin may be isolated by agitating with ether and evaporating the ethereal layer to dryness, and may be identified by its physical and sensible characters.

In the absence of free fatty acids, resin may be isolated from fixed oils by agitating the sample with moderately strong alcohol, separating the spirituous solution and evaporating it to dryness. It may also be isolated, and approximately estimated, by titrating the alcoholic solution of the sample with caustic alkali and phenolphthalein as described elsewhere. As the several acids which ordinary colophony contains are not present in constant proportion, the neutralising power of resin is variable, ranging from 0.310 to 0.430 gm. of colophony for 1 c.c. of normal alkali employed. The rosin subsequently extracted from the acidulated aqueous liquid, and left on evaporating the ethereal solution to dryness, is readily recognisable by the taste and smell on heating, and in favorable cases has the physical characters of rosin.

In the last method of operating, the resin is obtained in admixture

with any free fatty acids the sample may have contained. These modify the physical properties of the extracted resin very materially, and render the method useless for quantitative purposes. In such cases, if there is sufficient material for the purpose, a good indication of the relative proportions of fatty and resin acids in the mixture may be obtained by observing the density at the temperature of boiling water, as described on page 29. As, however, resin varies considerably in density and the fatty acids from various oils exhibit similar variations, the method furnishes but very rough results unless the source of the fatty acids be definitely known.

A method of separating fatty from resin acids based on the solubility of the barium salts of the latter in alcohol has been devised by Jean and modified by Rémont. Barfoed treats the sodium salts with ether-alcohol, which dissolves chiefly the resin acids. T. S. Gladding described a method of separating fatty and resin acids which is based on the ready solubility of silver resinates in ether, and the almost complete insolubility of silver oleate, &c. even in presence of a small quantity of alcohol.

All these methods have been superseded by that of Twitchell (J. S. C. I., 1891, 801), which, while not absolutely satisfactory, furnishes much more accurate results than the others. It is based upon the fact that aliphatic acids are converted into ethyle esters when acted upon by hydrochloric acid gas in their alcoholic solution, whereas colophony is said to undergo no change under the treatment, abietic acid separating from the solution.

The resin reacts acid in alcoholic solution with phenolphthalein, and unites readily with caustic potash to form a soluble soap. All that is necessary, therefore, is by the means indicated—to combine the fatty acids with alcohol, when the resin acids may be titrated with standard caustic soda solution, using phenolphthalein as indicator, or they may be combined with potash, and the resin soap thus formed separated from the saponified fatty esters by extracting with naphtha in a separating funnel.

The gravimetric method is carried out as follows. 2 to 3 gram of the mixture of fatty acid and resin are dissolved in ten times their volume of absolute alcohol in a flask and dry hydrochloric acid passed through in a moderate stream. The flask is set in a vessel with water to keep it cool. The acid is rapidly absorbed, and, after about forty-five minutes, the esters separate, floating in the solution, and no more hydrochloric acid is absorbed. The current of gas is stopped and the flask is allowed to stand for half an hour to complete the reaction. The liquid is diluted with about five times its volume of water and boiled until the acid solution is clear, the esters, with resin in solution, floating on the top. To this is added some naphtha and the whole transferred to a separating funnel, the flask being washed out with naphtha. The acid solution is then run off and the naphtha solution (which ought to measure about 50 c.c.) washed once with water and then treated in the funnel with a solution of 0.5 gram  $KIO_3$  and 5 c.c.

of alcohol in 50 c c of water and agitated. The resin is immediately saponified and the two layers separated completely. The solution of resin soap can then be run off, treated with acid, the resin collected in any manner desired, dried, and weighed. A second washing of the soap with naphtha is hardly necessary, as very little remains after the first extraction. The naphtha used is 74° gasoline, and for this purpose is to be preferred to ether.

The first stages of the volumetric method are similar to the gravimetric, with the exception that the contents of the flask are washed into the separating funnel with ether instead of naphtha, and the ether solution in the funnel is then thoroughly washed with water until the wash water is no longer acid, 50 c c of alcohol, previously neutralised, are then added and the solution titrated with standard caustic soda solution. If the combining equivalent of resin be known, its percentage may be calculated, or some of the original mixture may be also titrated, when the difference in caustic soda required will correspond to the fatty acids converted into ester.

Twitchell found that when 90 per cent of alcohol was used, instead of absolute alcohol, only 92 per cent of the fatty acids were converted into esters. If the alcoholic solution becomes heated by the passage of the hydrochloric acid, or if the solution be boiled without first diluting with water, the resin suffers change and requires less alkali to neutralise it.

That the results obtained by the above method are not absolutely correct, has been shown by Lewkowitsch (J. S. C. I., 1893, 504). The mean combining weights of different brands of commercial resin vary within considerable limits. The following results were obtained by Lewkowitsch by the examination of six different brands of American resin.

RESIN	1 GRM. REQUIRES CC. NORMAL KOH	ACID VALUE	COMBINING EQUIVALENT	MOLECULAR WEIGHT OF THE ANHYDROUS RESIN
No. 1, .	2.7470	154.11	364.03	710.06
No. 2,	2.8307	159.00	352.86	687.92
	2.8772	161.41	347.57	677.14
	2.9119	163.30	343.42	668.84
	2.9295	164.34	341.30	664.60
	2.9342	164.61	340.80	663.60
			348.33	

The average (348.33) agrees pretty closely with Twitchell's figure (346), but it is evident that rather widely differing results will be obtained, according to the particular sample that may have been used. Further, Lewkowitsch shows that under the action of the hydrochloric acid the resin appears to undergo some destruction with the formation of acids of lower molecular weights, since the volumetric analyses gave, as a rule, too high results. In the gravimetric process, again, some of these secondary products pass into the aqueous solution without being dissolved by the petroleum-ether. By a subsequent extraction with ether part of the dissolved substances may be recovered, but even then the results of the gravimetric analyses were found too low. Of course the unsaponi-



fiable oils occurring in resin remain in the petroleum-ether solution and thus escape being weighed. Lewkowitsch gives the following tables as indicating how nearly, in practical cases, the results obtained by either process approach the theoretical ones.

The "mixed fatty and resin acids" were obtained from soaps specially prepared on a large scale from carefully weighed quantities of fats and resins. Average samples of the fats and the resin were examined separately for the yield of fatty acids from the former and for the combining weight of the latter, these determinations being indispensable for a correct calculation of the theoretical amount of resin acids.

## VOLUMETRIC ANALYSIS

MIXED FATTY AND RESIN ACIDS	RESIN ACIDS	
	Theory	Experiment
	Per Cent	Per Cent
No 1, .	9.79	9.98, 9.31, 9.795, 9.91
2, .	19.69	23.97, 24.55, 23.93, 23.28, 23.98, 24.08
3, .	21.45	21.96, 21.78, 23.63
4, .	24.66	24.89, 25.15, 25.06, 24.23
5, .	30.31	29.69, 30.12, 28.18, 29.78
6, .	39.81	40.34, 40.37, 41.44, 42.13, 41.8, 40.37, 42.18, 40.55, 40.07, 40.05
7, .	45.05	45.78, 46.50, 49.61, 47.66, 46.45, 43.69, 41.12, 41.81, 40.77, 44.72, 47.84, 45.34, 44.24, 44.48, 44.39

## GRAVIMETRIC ANALYSIS

MIXED FATTY AND RESIN ACIDS	RESIN ACIDS	
	Theory	Experiment
	Per Cent	Per Cent
No 1, . . .	9.79	9.38, 9.97
2, . .	19.69	20.46, 20.55, 19.96, 19.99, 19.44, 19.33
3, .	21.45	19.25, 18.27, 19.37, 17.83, 19.54, 18.61, 18.67, 19.16
4, . . .	24.66	20.97, 16.65, 21.76
5, . .	30.31	25.76, 25.06, 23.66, 26.10
6, . . .	39.81	35.97, 38.86, 36.44, 36.14, 35.42, 35.86, 32.51, 36.29
7, . . .	45.05	37.58, 37.23, 37.29, 36.97, 35.32, 40.06, 36.8

By washing the petroleum-ether solution with alkali a second time, and

extracting the acid layer with common ether, the following results were obtained —

MIXED LATTY AND RESIN ACIDS	RESIN ACIDS				
	Theory	Experiments			
		Extracted by First Alkali Wash	Extracted by Second Alkali Wash	Extracted by Ether	Total
No.		Pct Cent	Pct Cent	Pct Cent	Pct Cent
2,	19 69	19 46	0 115	1 045	20 62
2,	19 69	18 44	0 074	0 822	19 34
3,	21 45	19 14	0 105	0 3615	19 607
3,	21 45	19 19	0 061	0 2839	19 54
4,	21 66	21 72	0 179	1 203	23 102
1,	24 66	22 29	0 239	1 01	23 54
5,	30 31	25 75	0 019	2 41	28 18
5,	30 31	26 97	0 085	0 72	27 73
6,	39 81	34 96	1 296	1 567	37 80
6,	39 81	34 696	0 190	1 12	35 91

Ulzer and Defres (abst. *Analyst*, 1897, 244) find that the acids of brown shellac gave by Twitchell's method 66 56 per cent of "resin acids" not converted into esters by the passage of hydrochloric acid through the alcoholic solution. By shaking out the petroleum spirit solution of the acids and esters with dilute sodium hydroxide an ester was obtained which formed a light yellow, semitransparent, resin-like mass which had a saponification number of 199 5.

The acids of an orange shellac having acid number 53 05 and saponification number 200 98 gave by Twitchell's process 72 89 per cent of resin acids which could not be esterified. The shellac acids appear to behave to some extent like fatty acids, since part of them form esters on being treated with hydrochloric acid gas in alcoholic solution.

Specimens of Angol-copal and Kauri-copal when examined by Twitchell's process show respectively 86 01 and 86 37 per cent of resin acids.

**Hydrocarbon Oils.**—The extensive production of various hydrocarbon oils suitable for lubricating purposes, together with their low price, has resulted in their being largely employed for the adulteration of animal and vegetable oils. The hydrocarbons most commonly employed are.—

1. Those produced from *petroleum* and by the distillation of *bituminous shale*.
2. Those produced by the distillation of common *rosin*, having the nature and properties detailed in the section on "Rosin Oil."
3. Neutral *coal oil*; being the portion of the products of the distil-

lation of coal-tar boiling above  $170^{\circ}\text{C}$ , and freed from phenoloid bodies by treatment with soda.

4 Solid *paraffin*, employed for the adulteration of beeswax and sperm-aceti, and used in admixture with stearic acid for making candles

The presence of hydrocarbons in fats and fatty oils is *detected* by the altered density of the sample, which is decreased by members of the first class, and increased by rosin and coal-tar products, by the lowering of the flashing and boiling point, by the fluorescence of members of the first two classes, and by the incomplete saponification by alkalies. The taste and odor on heating are also valuable indications.

Specific gravity is a character of some little value for detecting and approximately estimating hydrocarbons, but in practice the indications obtained are apt to be rendered valueless by the employment of a mixture which has the same density as the oil to be adulterated

The tendency of a hydrocarbon is to reduce the flashing and boiling point of the fixed oil, and in some cases a distinct separation may be effected by fractional distillation

Fluorescence is a character of considerable value for detecting the presence of hydrocarbons. If undoubtedly fluorescent, the sample certainly contains some hydrocarbon,<sup>1</sup> but the converse is not strictly true, as the fluorescence of some varieties can be destroyed by treatment, and some hydrocarbons have no fluorescence. Most of the hydrocarbons employed for lubricating purposes are strongly fluorescent, and the many others become so on treatment with an equal measure of strong sulphuric acid. A hydrocarbon possessing strong fluorescence may be evident in presence of a very large proportion of fixed oil, but if any doubt exist, the hydrocarbon should be isolated in the manner described on page 112. The fluorescence may usually be seen by holding a test-tube filled with the oil in a vertical position in front of a window, and looking at the sides of the test tube from above. A better method is to lay a glass rod, previously dipped in the oil, down on a table in front of a window, so that the oily end of the rod shall project over the edge, and be seen against the dark background of the floor. Another plan is to make a thick streak of the oil on a piece of black marble, or glass smoked at the back, and to place the streaked surface in a horizontal position in front of, and at right angles to, a well-lighted window. Either of these methods is better than the polished tinplate often recommended. The background

<sup>1</sup> Arcbutt states that genuine rape oil sometimes exhibits fluorescence. This may be due to the accidental presence of an insignificant proportion of mineral oil, as fluorescence becomes stronger with dilution of the fluorescent substance.

should be black, not white. Examined in this manner, very slight fluorescence is readily perceptible. If at all turbid, the oil should be filtered before applying the test, as the reflection of light from minute particles is apt to be mistaken for true fluorescence. In some cases it is desirable to dilute the oil with ether, to which an exceedingly small amount of mineral oil is sufficient to impart a strong blue fluorescence. This is useful in the examination of very dark oils, as the color is reduced without the intensity of the fluorescence being correspondingly decreased. If the oil be very dark, *e.g.*, a dark Gallipoli or brown rape oil, it should be first refined by agitating it successively with small proportions of concentrated sulphuric acid, water, and solution of sodium carbonate, and subsequently filtering. In some cases decolorisation may be effected by warming the oil and agitating it with freshly burnt animal charcoal, the liquid being subsequently filtered.

It must be borne in mind that the fluorescence is not perceptible by daylight, but may be brought out by burning a piece of magnesium ribbon in the proper position.

*The quantitative analysis* of mixtures of fat or fixed oils with hydrocarbons is best carried out by the following method, which combines rapidity, certainty, tolerable accuracy, and general applicability, and at the same time furnishes the hydrocarbons in a condition for further examination. The method has been thoroughly studied and largely used by the author —

The hydrocarbons which are to be determined are all unaffected by alkalis, whereas animal and vegetable oils and waxes undergo saponification. If potash or soda be employed, the resultant soap is soluble in water. The hydrocarbons, though insoluble in water and unaffected by alkalis, dissolve with greater or less facility in concentrated solutions of soap, and are very imperfectly separated on dilution. They may, however, be dissolved out from the dry soap by ether, chloroform, carbon disulphide, benzene, or petroleum spirit. In some cases a good separation is obtainable, but in others a considerable quantity of soap passes into solution, especially if the solvent be employed at a temperature approaching its boiling point. This tendency of the soap to undergo solution may be wholly avoided by treating the *aqueous solution* with the solvent, instead of 'exhausting the *dry soap*'

The following are the details of the manipulation — Five grm. of the sample are saponified by alcoholic alkali, the solution freed from alcohol,<sup>1</sup> and transferred to a separator of about 200 c.c. capacity,

<sup>1</sup> If the alcohol be completely eliminated, the ethereal layer is apt not to separate from the aqueous liquid at the next stage

furnished with a tap below and a stopper at the top. The tube below the tap should be ground or filed off obliquely, so as to prevent any liquid from remaining in it. The liquid is diluted with water till it measures from 70 to 100 c.c. From 50 to 60 c.c. of ether should next be added, the stopper inserted, the liquids thoroughly shaken and allowed to rest for a few minutes. As a rule, two well-defined layers will form, the lower one brownish, consisting of the aqueous solution of soap, the upper of ether, containing any hydrocarbon in solution. Separation does not always occur readily, the liquid remaining apparently homogeneous, or assuming a gelatinous consistency. In such cases, separation may be induced by thoroughly cooling the contents of the separator; by adding caustic potash solution; by adding more ether and reagitating, or, if all these means fail, a *few* cubic centimetres of alcohol may be added, and a gentle rotatory movement imparted to the liquid, avoiding complete admixture, when a very rapid separation of the ethereal layer almost invariably occurs. The aqueous liquid is then run through the tap into a beaker. About 10 c.c. of water and a few drops of caustic alkali solution are added to the ether which remains in the separator, and the whole agitated. The washings are then run off in their turn, and after repeating the treatment with water, which is removed by the tap as before, the ethereal solution is poured off through the mouth into a tared flask. The aqueous liquid and washings are then returned to the separator, and agitated with a fresh quantity of ether, which is washed and poured into the flask as before. The agitation of the soap solution is repeated once more, when the extraction of the hydrocarbon oil will be complete. The ethereal solution will usually be strongly fluorescent. The flask containing it is attached to a condensing arrangement, and the greater part of the ether distilled off by immersing the flask in boiling water. When distillation has ceased, the condenser is detached and the flask placed on the top of the water-oven, by which the rest of ether is soon dissipated. Sometimes the hydrocarbon will contain globules of water, in which case the flask should be held horizontally, and rotated rapidly, so as to spread the oil over the sides in a very thin layer, and facilitate the evaporation of the water. When no more water is visible, and the smell of ether is scarcely perceptible, the flask is placed on its side in the water-oven for ten or fifteen minutes and



FIG. 8

weighed,<sup>1</sup> when the increase of weight over the original tare gives the amount of hydrocarbon oil extracted. Prolonged heating should be avoided, as many hydrocarbons are sensibly volatile at 100° C. This is notably the case with coal tar oil, and hence, in analysing mixtures containing it, the heating in the water-oven should be wholly dispensed with. With rosin oil, paraffin wax, and the denser mineral oils there is but little danger of loss by volatilisation at 100° C.

The foregoing process has been extensively employed by the author, and has been proved to be accurate on numerous mixtures of fatty oils with hydrocarbon oils. The results obtained are correct to within about 1 per cent in all ordinary cases.<sup>2</sup> In cases where extreme accuracy is desired, it is necessary to remember that most, if not all, animal and vegetable oils contain traces of matter wholly unacted on by alkalis. In certain cases, as butter-fat and codliver oil, this consists largely of cholesterol,  $C_{26}H_{44}O$ , which may be obtained in characteristic crystalline tablets by warming the ethereal extract with alcohol, and allowing the solution to cool. The proportion of unsaponifiable matter soluble in ether which is naturally present in fixed oils and fats, rarely exceeds 1½ per cent, and is usually much less. Sperm and bottlenose whale oils, however, constitute an exception, yielding about 38 to 40 per cent. of matter soluble in ether. This peculiarity has little practical effect on the applicability of the process, as sperm oil being among the most valuable of commercial fixed oils, it is rarely present without due acknowledgment of the fact. An unknown oil may be recognised as sperm or bottlenose oil by the characters detailed in the section relating to them.

Spermaceti and the other waxes yield after saponification large percentages of matter to ether, and hence the process is not available for the determination of paraffin wax in admixture with these bodies, though it gives accurate results with the mixtures of paraffin and stearic acid so largely employed for making candles.

<sup>1</sup> Sometimes it is very difficult to obtain a constant weight by the means indicated in the text. In such cases, instead of heating the flask on the water-oven, it should be kept on the bath of boiling water and a moderate current of air, filtered by passing it through a tube containing cotton-wool, should be blown through it by a second tube passing through the cork. The fittings are then detached, and the flask heated for a short time in the water-oven.

<sup>2</sup> Traces of fatty oils which had escaped saponification and traces of soap are apt to pass into the ethereal solution, and hence the proportion of unsaponifiable matter found is often slightly reduced on treating the ether-residue with alcoholic potash, and again extracting the solution of the soap with ether.

The following table indicates the behavior of the constituents of complex mixtures of fats, oils, and waxes when the aqueous solution of the saponified substance is shaken with ether:—

DISSOLVED BY THE ETHER	REMAINING IN THE AQUEOUS LIQUID
Hydrocarbon Oils, including Shale and Petroleum Oils, Rosin Oil Hydrocarbons, Coal tar Oil, Paraffin Wax and Ozokerite, Vaseline	Fatty Acids
Neutral Resins.	Resin Acids
Unsaponified Fat or Oil	Carbolic and Cresylic Acids, and other phenols
Unsaponifiable matter, as Cholesterol, from liver oils, &c	In the form of potassium salts
Dodecyl Alcohol, from sperm and Bottlenose Oils	
Cetyl Alcohol, from Spermaceti	Glycerol (Glycerin).
Myristyl Alcohol, from Beeswax	Excess of Caustic Potash.
Coloring matters, as from Palm Oil	

The hydrocarbon having been isolated by saponifying the sample and agitating with ether, its nature may be ascertained by observing its specific gravity, taste, and smell, behavior with acids and bromine. If the proportion be small, it may be necessary to operate on a larger quantity than 5 grm. of the sample. A good approximation of the specific gravity of the extracted hydrocarbons may be made on Hagen's principle, by adding a drop of the oil to very dilute alcohol, or ammonia, and adjusting the strength of the liquid so that it may be identical with that of the drop of oil. The specific gravity of the dilute alcohol is then ascertained in the usual way. The fluorescence of hydrocarbons is best observed in the manner described on page 111. It often becomes intensified by treating the extracted hydrocarbon with an equal measure of strong sulphuric acid.

The smell and taste of the hydrocarbons are often highly characteristic of their origin. The smell of coal-tar oil is readily observed, and the taste, especially the after taste, of rosin oil is not to be mistaken. The smell produced on strongly heating a drop of the oil in a platinum capsule is also highly characteristic. Further details respecting the tests for hydrocarbons are given in the section on "Mineral Lubricating Oils."

The *higher alcohols* from sperm and bottlenose oil may be separated from hydrocarbons by treating the ether-residue with rectified spirit,

which dissolves the alcohols without notably affecting the hydrocarbons.

If the aqueous liquid separated from the ethereal layer be treated with dilute sulphuric acid, the fatty acids are liberated, and may be weighed, titrated with standard alkali, or otherwise examined.

When it is merely desired to ascertain approximately the proportion of hydrocarbon oil in a mixture, and not to isolate it and examine it further, there is no occasion to extract the solution of the saponified oil with ether. Instead, the aqueous liquid may be at once acidulated with dilute sulphuric acid, a little ether added to promote the separation of the mixed hydrocarbon oils and fatty acids, the aqueous liquid tapped off, and the oily layer repeatedly agitated with water till the washings are no longer acid to litmus. Rectified spirit and a few drops of phenolphthalein solution are then added, and the liquid titrated with decinormal alkali. The oleic acid thus deduced, multiplied by 1.053, gives the amount of saponifiables, and the difference may be regarded as unsaponifiable matter. The latter represents the hydrocarbons, and the former the fat or fixed oil of the mixture, provided that waxes, including sperm and bottlenose oils, are absent.

When the nature of the fat or oil is known, and it is merely desired to estimate the proportion of hydrocarbon present, and not to ascertain its exact character, a very fair approximation to the truth can be obtained by ascertaining the saponification equivalent of the sample.

The table on page 117 gives an outline of the processes described in the foregoing section.

## IDENTIFICATION OF FIXED OILS.

The recognition of an unmixed fat or fixed oil may usually be effected by a careful application of the methods of examination already described. Systematic schemes for the purpose have been devised, but can not be implicitly relied on, owing to the variable nature of the bodies themselves. The color reactions are of little value, unless confirmed by the indications of other tests.

In examining fats and oils for the detection of adulteration, the relative commercial value of the different kinds should be kept in view. In addition to the adulteration of the more valuable bodies with the cheaper, the use of hydrocarbon from distillation of petroleum, shale, coal, and rosin, is also extensively practised.



# EXAMINATION OF OILS CONTAINING FOREIGN ADMIXTURES

From 5 to 10 gm. weight of the sample (previously melted by warming if necessary) is passed through a dry filter, unless already perfectly clear	
<p><b>Residue may contain</b> no notable ash on ignition, thus proving the absence of most of the compounds, the following trace amounts with water and dilute <math>H_2SO_4</math> may be advantageously separated: <i>lead, sand, and insoluble matter.</i></p> <p><b>Do not</b> generally contain any of the following: <i>water, ether, alcohol, sulphide, and leave the clear oil is agitated in a tapper separator with water and ether. The aqueous solution is separated, and the oil solution again shaken with ether if the previous treatment was found to remove anything.</i></p>	<p><b>The Clear oil</b> (N. B.—If an aliquot portion of the clarified oil be not blackened when shaken with alcohol and ammonium sulphide, and leave the clear oil is agitated in a tapper separator with water and ether. The aqueous solution is separated, and the oil solution again shaken with ether if the previous treatment was found to remove anything.)</p>
<p><b>Aqueous liquid</b> contains soap, and is separated by adding water. It is separated to the dryness of the residue, and the residue is further dried by the addition of a little anhydrous <math>CaCl_2</math> or <math>P_2O_5</math>. If still orange, and the characteristic blue color is not obtained, the oil is again dried by the addition of a little anhydrous <math>CaCl_2</math> or <math>P_2O_5</math>.</p>	<p><b>Oil solution.</b> Agitate with dilute <math>H_2SO_4</math> and separate. Wash residual oil repeatedly by agitation with water till the aqueous liquid no longer reddens litmus.</p>
<p><b>Acid liquid may</b> contain sulphides of metals previously extracted with ether, and the oil is dried by the addition of a little anhydrous <math>CaCl_2</math> or <math>P_2O_5</math>. If still orange, and the characteristic blue color is not obtained, the oil is again dried by the addition of a little anhydrous <math>CaCl_2</math> or <math>P_2O_5</math>.</p>	<p><b>Solution of oil in ether.</b> Add a few drops of phenolphthalein solution. Then gradually, with repeated shaking, a solution of 2 ccs. of <math>NaOH</math> in 10 c.c. anhydrous spirit, 90 of water, in quantity some what greater than is sufficient to produce a permanent red color. Then separate the undissolved oil without shaking. Agitate the oil and aqueous liquid respectively with slightly alkaline water and with ether, and add the washings to the oil in small quantities.</p>
<p><b>Aqueous liquid</b> Add methyl orange, and then dilute. If <math>H_2SO_4</math> till acid reaction is obtained. If still orange, and the characteristic blue color is not obtained, the oil is again dried by the addition of a little anhydrous <math>CaCl_2</math> or <math>P_2O_5</math>.</p>	<p><b>Oil.</b> Evaporate off ether and spoutify residual oil by alcoholic potash. Boil off alcohol, dissolve soap in warm water, and agitate cooled solution with water and ether. Wash residual oil with water and ether time with ether. (In analysis of waxes, treatment of the dry soap with boiling toluene should be substituted for agitation of the solution with ether.)</p>
<p><b>Only layer consists</b> of insoluble, fatty acids, and is separated by the addition of a little anhydrous <math>CaCl_2</math> or <math>P_2O_5</math>. If still orange, and the characteristic blue color is not obtained, the oil is again dried by the addition of a little anhydrous <math>CaCl_2</math> or <math>P_2O_5</math>.</p>	<p><b>Aqueous liquid</b> contains <i>glycerol and soap</i>, formed by saponification of fatty acids, and is separated by the addition of a little anhydrous <math>CaCl_2</math> or <math>P_2O_5</math>. If still orange, and the characteristic blue color is not obtained, the oil is again dried by the addition of a little anhydrous <math>CaCl_2</math> or <math>P_2O_5</math>.</p>
<p><b>Aqueous liquid</b> Distill to small bulk, turning discolored by barium hydroxide, and weigh barium salts of total fatty acids. No ester is soluble in water, and the residue is when neutralized by <math>NaOH</math> and evaporated and ignited.</p>	<p><b>Ethereal liquid</b> evaporated at 100° leaves a residue which, when weighed, and may contain <i>hydrocarbons, esters, alcohols, ethers, aldehydes, and color-</i></p>

In practice it is often of less importance to know the origin of a sample than whether it may be used as a substitute for the genuine oil. This may be ascertained with tolerable certainty and in some cases the nature of the adulterants definitely detected.

It is not possible to give a general scheme available for the identification of any unmixed fat or fixed oil, but the examination may be conducted on a systematic plan. By the following method identification may generally be effected, and much information gained that will suggest the special tests for the bodies suspected to be present —

1. Place a drop of the oil on the back of the tongue by means of a glass rod and taste it carefully, avoiding too hasty a decision. In this manner marine animal oils, linseed, croton, mineral, rosin, and some other oils may often be detected. Rosin oil is remarkable for the nauseous after taste produced by it. Rancidity may also be recognised by taste.

2. Heat a portion of the sample in a porcelain or platinum capsule to about  $140^{\circ}$  or  $150^{\circ}$  C, and observe the odor carefully. When sufficiently cool, pour a little into one hand, rub with the other, and smell again. A little practice will allow of vegetable oils being readily distinguished from animal oils, and the products of fish and marine mammals from those of terrestrial animals. The odor on heating will also frequently permit the recognition of mineral and rosin oils, and, if the remainder of the sample be strongly heated till it ignites and the flame then blown out, the vapors will often have a characteristic odor.

3. Ascertain the specific gravity of the sample at  $15.5^{\circ}$  C if fluid at that temperature, but at the boiling point of water (page 29) if solid at the ordinary temperature. This test is valuable, but if the sample be very old, or a mixture of several bodies, or if much free acid be present, the indications are less reliable. The tables on pages 119 and 120 will enable an unmixed substance to be arranged in one of nine groups. More precise figures are given in the tables on page 91 *et seq*.

Sperm and bottlenose oils are readily distinguished from shale and petroleum products of similar density by the elaidin test, the determination of their saponification-equivalents, and the quantitative results of their saponification. Their determination when mixed with hydrocarbon oils may be effected as described under "Sperm Oil." Oleic acid is distinguished from hydrocarbons by its solubility in an aqueous solution of caustic soda. Mixtures of oleic acid and hydrocarbons may be analysed by titration with standard alkali. If fixed oils be present, the methods given on page 117 should be used.

## OILS.

SUBSTANCE.	SPECIFIC GRAVITY AT 15° TO 16° C				
	875 to 884	884 to 912	912 to 920	920 to 937	937 to 970
Vegetable Oils,	None	None.	Olive Almond Arachis Rape and Colza Mustard Non-drying oils	Cotton- seed Sesame Sunflower Hazelnut Poppyseed Hempseed Linseed (raw) Walnut Coconut oleum	Japanese wood. Croton Castor. Boiled lin- seed. Blown oils.
Terres- trial Animal Oils,	None.	None.	Nentsfoot Bone Lard oil. Tallow oil	None	None
Marine Animal Oils,	Sperm Deglug Bottle- nose	None	.	Whale. Porpoise Seal Menhaden Cod liver. Shark-liver	None.
Free Fatty Acids,	None	Oleic acid	.	Linolic acid	Ricinic acid
Hydro- carbons,	Shale products Petrol- eum products	Shale products. Petrol- eum products	Heavy petroleum products	Heavy mineral oil.	None

## FATS

SUBSTANCE	SPECIFIC GRAVITY AT 55° TO 100° C			
	750 to 800	800 to 855	855 to 863	863 to 877
Vegetable Fats,	None	None	Palm oil Cacao butter	Palmnut oil Coconut oil Japn "wax" Myrtle "wax" Cottonseed stearin
Animal Fats,	None	None.	Tallow Lard Suet Dripping. Bone fat Margarine.	Butter fat Compound lard

## WAXES

SUBSTANCE	SPECIFIC GRAVITY AT 98° TO 100° C			
	750 to 800	800 to 855	855 to 863	863 to 877
Vegetable and Animal Waxes,	None	Spermaceti Beeswax Chinese wax Carnauba wax	None.	None
Free Fatty Acids,	None	Stearic acid Palmitic acid Oleic acid.	None	None.
Hydrocarbons,	Paraffin wax Ozokerite	Shale and petroleum products	Vaseline.	...

The hydrocarbon oil produced by the distillation of rosin is not included in these tables, as its high density ( 970 to 1 000) places it outside any of the classes. The same remark applies to rosin itself, which is somewhat denser than water, and to coal-tar products of high boiling point which might be mistaken for, or found mixed with, the fixed oils.

The non-drying vegetable oils are distinguishable from the similar oils of animal origin by their taste and odor on heating. The melting points of the acids from animal oleins are much higher than those prepared from the vegetable non-drying oils. Many of the vegetable oils show absorption-spectra which is never the case with animal oils. The vegetable non-drying oils may be distinguished from each other by various tests. Rape and mustard oils are distinguished from others by insolubility in glacial acetic acid and by high saponification-equivalents. Bone oil usually gives an orange or reddish-yellow elaidin of a pasty consistence, while lard oil and tallow oil yield a firm product of a pale or lemon-yellow color. The product from neatsfoot oil is variable.

The acids from the moderately drying oils, especially cottonseed, solidify at a much higher temperature than those from the strongly drying oils, and the same distinction applies, though in a less-marked manner, to the oils themselves.

The oils possessing drying characters may be in a great measure differentiated by their specific gravities and viscosities. The elaidin-test and color-reactions furnish further means, to which may be added the solubility in glacial acetic acid, rise of temperature with sulphuric acid, iodine-absorption, and melting and solidifying points

of the acids. The figures ordinarily yielded by those methods of examination are expressed in the following table:—

OIL	TURBIDITY-TEMPERATURE (VALENTA)	TEMPERATURE WITH SULPHURIC ACID (MALLINÉ)	IODINE ABSORPTION (HÜBL)	FATTY ACIDS (HÜBL)	
				Melting Point	Solidifying Point
Cottonseed,	87 to 110	67 to 75	105 to 109	37.7	30.5
Sesame,	87 to 107	67 to 70	103 to 105	26.0	22.3
Nigerseed,	49	81 to 82	133	26.0 <sup>1</sup>	
Poppyseed,	...	86 to 88	134 to 137	20.5	16.5
Hempseed,	.	98	143	19.0	15.0
Linseed,	57	103 to 111	155 to 160	17.0	13.3
Walnut,	.	101	142 to 144	20.0	16.0

Coconut olein is distinguished from other vegetable oils by its low saponification-equivalent and the very moderate heating produced by sulphuric acid.

The marine animal oils may be distinguished as a class by their fishy smell and taste; by the red or reddish-brown color obtained on saponifying them; and by the darkening that ensues on passing a current of chlorine through them. They may be differentiated by their saponification equivalents, behavior with acetic acid, rise of temperature with strong sulphuric acid, and other tests.

The color-test with sulphuric acid is useful. Porpoise oil and some varieties of whale oil contain a notable proportion of esters of lower acids, and give characteristic results with the distillation-test.

Oils of specific gravity above .937 are few and easily distinguished. Croton and castor oil are purgative and readily soluble in rectified spirit, but have little further resemblance. Boiled linseed oil and Japanese wood oil have specific gravities between .937 and .950, dry rapidly on exposure, and give a firm brown or black clot with sulphuric acid. Blown oils closely resemble castor oil, but may be distinguished as described in the section treating of that oil. Rosin oil has a specific gravity exceeding .970, and is not saponified to any considerable extent by alkalis. It is readily identified by its strong after-taste, and the terebinthinous odor developed when the sample is heated till it catches fire, and the flame then blown out. Mixtures of rosin oil with fatty oils may be analysed as described on page 112.

<sup>1</sup> This figure is not due to Hübl, but is the mean of several determinations by L. Archbutt. Hübl's melting and solidifying points were determined by introducing the fatty acids into a narrow test-tube, gently agitating with a thermometer, and noting the point at which the whole contents become either quite clear or slightly cloudy.

The following table shows the behavior of the principal fish oils with important tests. For comparison, sperm and bottlenose oils are included in the table.

OIL	SAPONIFICATION-EQUIVALENT	TURBIDITY-TIMBLE-TUBE	TIMBER-TURN WITH SULPHURIC ACID	HALOGEN-ABSORPTION		
				Bromine	Iodine	
					Br $\times \frac{1.27}{80}$	Direct
Sperm. .	380 to 454	98	45 to 47	56	89	84
Bottlenose, .	419 to 456	102	41 to 47	49	78	80
Whale, .	250 to 296	31 to 83	85 to 91	51	81	
Porpoise, .	256 to 260	40	50			
Seal, .	286 to 296	72	92	57 to 60	91 to 95	
Menhaden, .	292	64	123 to 128			1-18
Cod-liver, .	303	79 to 101	103 to 116	81 to 87	129 to 138	
Lang-liver, .	-			82	131	
Haddock-liver, .	-			110	175	
Skate-liver, .	-		102	109 to 123	173 to 195	
Shark-liver, .	316 to 400	105	90	84	134	

The solid hydrocarbons having a density below .800 at the boiling point of water are described under "Paraffin Wax."

The distinctions between the various waxes are fully indicated in the table on page 102, and in the special sections on "Spermaceti," "Beeswax," and "Carnauba Wax." Free acids are at once distinguished from the waxes by their solubility in alcohol, behavior with alkalis, and their saponification equivalents, from each other by their melting points and combining weights. Vaseline and similar hydrocarbons are sharply distinguished from the waxes and fatty acids by being incapable of saponification.

The vegetable fats of low specific gravity are somewhat numerous and have not been much studied, but few of them are common. The color, taste, and odor suffice to distinguish many of them, and further information is afforded by Valenta's acetic acid test and the determination of their melting and solidifying points. The animal fats may be distinguished by similar means.

The vegetable fats of high specific gravity are readily differentiated. Coconut and palmnut oils are soft, melt readily, and have low saponification-equivalents. Japan and myrtle wax are hard, wax-like bodies of comparatively high melting point. (See "Japan Wax.") Palmnut oil is distinguished from coconut oil and coconut stearin by its taste and smell. Butter-fat is the only fat of animal origin (except wool

fat) having a specific gravity higher than .863. Its odor, taste, and behavior with Reichert's test are highly characteristic.

The nature of the sample having been indicated, further confirmation may be obtained by means of the tables commencing on page 91. The principal fats, oils, and waxes are described at greater length in the following sections.

In the case of a sample consisting of a *mixture of wholly unknown bodies*, identification of the constituents is often a difficult problem, but when the leading component is known or can be recognised, the detection of the others becomes more feasible. In most cases oils cannot be recognised by distinct and specific tests, such as exist for the different elements, and in arriving at a conclusion as to the composition of any sample of mixed oils the analyst must be content to be guided in a great measure by circumstantial evidence and a careful consideration of probabilities. The foregoing methods of examination are of course employed, and in addition such special tests as will be found described under the various heads. The sub articles descriptive of the more important substances contain a list of the admixtures most commonly found in each and special tests suitable for its detection.

The following facts are important in the examination of complex samples, and to a less extent for the identification of unmixed ones.

Much information may be obtained by determining the products formed by saponification. Thus most fixed oils and fats yield a soap and glycerol, but sperm oil and the waxes yield products differing from glycerol in being insoluble in water but soluble in ether. Sperm the bottlenose oils only yield about 63 per cent of fatty acids, while most other fixed oils (not the waxes) give about 95 per cent. Butterfat, porpoise oil, and the oils from coconut and palmnut yield a notable proportion of acids which are volatile or soluble in water, but in the case of almost all other fats and oils the acids are practically insoluble. Resin gives nearly 100 per cent of resin acids and no glycerol, mineral and rosin oils do not undergo saponification, and can be dissolved out of the soap solution by agitating with ether.

The physical properties and combining weights of the acids afford important information. The acids from rape and castor oils neutralise sensibly less alkali than those from most bodies of this group. Lard, tallow, and neatsfoot oils yield acids of much higher melting point than the non-drying vegetable oils which they resemble. Cottonseed oil yields acids solid at the ordinary temperature, while most drying and semi drying oils yield liquid acids. Any admixture of resin acids

tends to increase the specific gravity of the fatty acids, at the same time lowering the melting point. When it is intended to examine the character of the acids, it is highly important that the aqueous and alkaline solution of the soap should be previously agitated with ether until nothing more is removed, as any admixture of wax or hydrocarbon would profoundly modify the properties of the acids.

The details of the method of separating these admixtures and of determining the fatty acids will be found elsewhere.

The drying oils are heavier but less viscous than the non-drying oils, apparently in proportion to their drying tendency. The non-drying oils give solid elaidin, the product becoming less and less firm as it is derived from a more strongly drying oil. Similarly, the heating produced by mixture with sulphuric acid, the solubility in glacial acetic acid, and the iodine-absorption appear to bear a direct relationship to the drying properties of a vegetable oil. By a careful application of these facts an approximate estimate of the proportions of different oils in a mixture can often be made.

## SPECIAL CHARACTERS AND MODES OF EXAMINING FATS, OILS, AND WAXES.

### Olive Oil.

*French*—Huile d'olive. *German*—Olivenöl.

(See also p. 91.) Olive oil is extracted from the fruit of the olive by pressure or by solution in carbon disulphide.<sup>1</sup>

<sup>1</sup> Of the commercial varieties, Provence and Tuscan oils are among the most esteemed. The finest grade in the market is "finest cream sublime oil," which is imported from Leghorn. Oils of other origin, in the order of their commercial value, are "Sublime," Gallipoli, Sicilian, Spanish, Portuguese, Levant, and Mogador. That imported from Sfax, on the coast of Tunis, as well as that sold in the so-called "Florence flasks," is usually of inferior quality. Lucca and Gallipoli oils are well-known brands, and much excellent oil is expressed in Spain, and exported from Malaga and Seville. Much olive oil is now prepared in California.

The variations in the quality are largely dependent on the manner in which the olives are treated, as, e.g., the care with which the fruit is plucked, the length of time it is stored before being crushed, and other conditions which affect the color, smell, and appearance of the oil expressed.

In some countries olive oil is an important article of diet. It is employed in the manufacture of woollen cloth, and in dyeing fabrics turkey-red, though its application for these purposes is decreasing. The inferior varieties are employed in soapmaking. It is highly esteemed as a lubricant, and is largely employed when price permits. The quantity used in this way depends much on the price of rape oil, which is usually much cheaper, and, though more liable to "gum" than olive oil, is less apt than the latter to become rancid.



Olive oil varies somewhat in its physical characters according to its quality. The finest kinds have a pale yellow color, with a tinge of green, are almost wholly free from odor, and possess a mild and agreeable taste. Inferior qualities have a greenish-yellow or brownish-yellow color, an unpleasant odor, and a decidedly acrid after-taste.

The absorption-spectrum of the fresh oil shows well-defined chlorophyll bands, which become changed or altogether destroyed on exposure to sunlight or heating with caustic alkali.

When cooled to about  $10^{\circ}\text{C}$ , it deposits a white granular fat. At  $0^{\circ}$  it solidifies to a product which can be separated by pressure into a solid tallow-like fat, consisting chiefly of palmitin, and about 70 per cent. of a fluid composed of olein with some linolin. Traces of cholesterol are present, and usually more or less free oleic acid. By saponification olive oil yields glycerol and oleates, palmitates, and small quantities of arachidates and linolates.

Olive oil is the type of a non-drying vegetable oil. It does not thicken materially, even on prolonged exposure to air, but gradually becomes rancid, a change which appears to be dependent in great measure on the presence of certain albuminous and mucilaginous matters.

The specific gravity ranges from about .914 to .917. Commercial samples, expressed at a high temperature, may have a specific gravity as high as .925 by reason of the increased proportion of palmitin. Such oils are usually dark in color. Samples containing much free acid have the lowest gravity.

If free from acid it is only slightly soluble in alcohol, but dissolves in about  $1\frac{1}{2}$  times its weight of ether, and is miscible in all proportions with carbon disulphide, chloroform, and hydrocarbons.

When heated to about  $120^{\circ}$  olive oil becomes lighter, and at  $220^{\circ}$  nearly colorless and at the same time rancid. At  $315^{\circ}$  it suffers decomposition, emitting a disagreeable odor of acrolein.

The following are some observed analytic data of the mixed fatty acids of olive oil:—

Specific gravity at $99^{\circ}\text{C}$ (water at $15.5^{\circ} = 1$ ),	843	(Allen)
" " " $100^{\circ}\text{C}$ (water at $100^{\circ} = 1$ ),	8749	
Solidifying point (liter test),	$16.9^{\circ}$ to $28.4^{\circ}\text{C}$	(Lewkowitsch)
Melting point,	$19^{\circ}$ to $28.5^{\circ}\text{C}$ .	
Saponification value (mgrm KHO),	193	(Theoerner.)
Iodine value,	86 to 90	
Refractive index,	1.441	(Theoerner.)

### ASSAY OF GENUINE OLIVE OIL

Genuine olive oil often contains a notable quantity of free acid, the proportion of which increases by keeping and exposure. In 89 samples intended for lubrication, and known to be genuine, Archbutt found proportions of free acids (calculated as oleic) ranging from 25.1 to 2.2 per cent, the average being 8.05 per cent. He found that more than 5 per cent of free acid renders the oil unsuitable for burning, causing a serious charring of the wick. Oil intended for table use should contain little free acid, but for soap-making it is no detriment, and for turkey-red dyeing a very acid oil is preferred. The proportion of free acid in olive oil can be ascertained with ease and accuracy by titration in presence of alcohol with standard caustic alkali and phenolphthalein, in the manner already described.

Burstyn (*Dingl. polyt. J.*, cxvii, 314, *Jour. Chem. Soc.*, xxix, 789) has described the following method for estimating the free acid in olive oil. The process appears well suited for rapid technical investigations, though the volumetric method described elsewhere will be preferred by chemists. The oil is shaken with an equal measure of rectified spirit of '830 to '840 specific gravity, the exact figure being accurately determined. After the liquids have separated, the specific gravity of the spirit is determined. Burstyn finds that an oil, 100 c.c. of which contains free acid in quantity sufficient to neutralise 1 c.c. of normal alkali ( $= .282$  per cent. of oleic acid), will raise the gravity of the alcohol from '830 to '8325, and that each additional 1 c.c. of alkali neutralised corresponds to an increase of .0003 in the density of the spirit. Hence the increase due to the solution of a trace of neutral fat is .0022, and that each increase of .0001 in specific gravity beyond this number represents  $.282 \div .0022 = .094$  gm. of free acid per 100 c.c. Burstyn states that the action of olive oil on brass is regularly and directly proportional to the percentage of free acid present.

In examining oil intended for cooking or table use, the flavor and odor should be carefully observed, as many apparently genuine specimens which are fairly free from acid are unsatisfactory in this respect.

### EXAMINATION OF OLIVE OIL FOR ADULTERANTS.

Olive oil is very liable to adulteration, the sample being sometimes colored to give it the appearance of green olive oil. Cottonseed oil is perhaps the most frequent adulterant; but arachis, sesame, poppy, and rape oils are also used. Poppy oil is said to be a favorite addition, on account of its sweet taste and slight odor. Fish oils are occasionally

employed, menbaden oil being said to be used frequently. Lard oil is largely used when the price permits of it, "superfine Lucca oil" being stated sometimes to contain as much as 60 to 70 per cent Hydrocarbons are also used.

In the United States cottonseed oil is largely sold under the name of olive oil. In fact, the label "Huile d'olive vierge, E Loubon, Nice," is generally understood in the grocery trade to indicate cottonseed oil.

In examining olive oil, the most important indications are the specific gravity, the solidifying point, the saponification equivalent, the iodine absorption, the rise of temperature on treatment with sulphuric acid and with bromine, the elaidin test, Livache's test, and certain color-reactions. Some sophistications require the application of special tests for their detection.

The specific gravity of olive oil varies very sensibly with the quality, the most acid specimens having the lowest specific gravities. The range allowed by the German and United States Pharmacopoeias is between .915 and .918, at 15° C. Of upwards of eighty samples of genuine olive oil examined by Archbutt, the specific gravity at 15.5° C., compared with water at the same temperature, never exceeded .917, and was rarely as high. The lowest gravity observed was .9136, the sample containing 24.5 per cent of free oleic acid. Hence it is evident that the proportion of free acid should be taken into account in judging the character of olive oil from its gravity. Taking the density of genuine neutral olive oil as .917, it appears that each 5 per cent of free acid diminishes the specific gravity of the sample by about .0007. Adulteration of olive oil with *rape oil* will tend slightly to reduce the gravity of the sample, whilst addition of the oils of Groups III. and IV. will increase it. A judicious admixture of rape and cottonseed oils will not affect the gravity of the sample, but the presence of any considerable proportion of rape oil will sensibly raise the saponification-equivalent of the sample.

The iodine absorption is a valuable means of detecting adulterations of olive oil. Genuine samples usually show an absorption varying from 81 to 85 per cent. California oils give higher figures. Blasdale has found absorptions of from 80.4 to 86.5, and Langfeld and Paparelli 77.2 to 88.6 per cent. Rape, sesame, and cottonseed oils all assimilate upwards of 100 per cent, and poppyseed, hempseed, and linseed oils from 134 to 160 per cent. Arachis oil is not so distinctly indicated.

The rise of temperature on treating the sample with sulphuric acid,

or with bromine, are valuable indications of the purity of olive oil. Almost all oils, except coconut olein and tallow and lard oils, produce more heat than olive oil, so that a rise of temperature with sulphuric acid of more than  $44^{\circ}\text{C}$ . may at once be considered as indicating probable adulteration, and in some cases it allows of an approximate estimation of the extent of the sophistication.

Archbutt (*J. S. C. I.*, 1897, 309) has determined the heat of bromination of ten samples of olive oil, and gives figures ranging from 13.55 to 14.5.

The elaidin test is also of great value. Pure olive oil yields in less than two hours, at from  $15$  to  $20^{\circ}\text{C}$ ., a mass that cannot be displaced by shaking the bottle, and in twenty-four hours a solid and spongy, pale yellow or nearly white mass is produced. With adulterated samples, the elaidin is orange or dark red, and liquid or semi-solid. Not unfrequently a liquid layer is formed on the surface of the solid elaidin. The test is applicable to the detection of sesame, rapeseed, cottonseed, poppyseed (as little as 5 per cent.), linseed, and other oils of Groups II and III when in admixture with olive oil. Exposure to air under the conditions prescribed on page 68 is also a test for an admixture of the drying oils.

The rise of temperature and the results of the elaidin test are much less marked when the oil has been long exposed to sunlight.

The melting and solidifying points of the fatty acids will often allow the nature and proportion of an admixture with olive oil to be inferred, and O. Bach has suggested the use of J. David's process of separating stearic and oleic acids for detecting adulterants. According to Bach, if 1 c.c. of the fatty acids from genuine olive oil be treated with 15 c.c. of David's alcoholic acetic acid, perfect solution takes place at the ordinary temperature, but the acids from cottonseed oil are insoluble, and the solution obtained by warming the liquid gelatinises when cooled to  $15^{\circ}\text{C}$ . The acids from sesame and arachis oil are stated to behave similarly, while those from sunflower oil dissolve on warming, but separate as a granular precipitate at  $15^{\circ}\text{C}$ . The acids from rape oil are completely insoluble and float on the surface of the liquid. Olive oil containing 25 per cent. of sesame or cottonseed oil yields acids which form a granular precipitate, but smaller proportions cannot readily be detected.

For detecting the admixture of *cottonseed oil*, the specific gravity, iodine number, bromine and sulphuric acid thermal values, Livache's, Becchi's and Halphen's tests and the nitric acid color test (see "Cottonseed Oil") are available.

*Sesame oil* may be detected by the modified Baudouin test. (See "Sesame Oil.")

Several observers have noted that certain varieties of olive oil containing coloring matter from the aqueous part of the pulp of the fruit give a rose color with the hydrochloric acid-furfural test, but that by applying the test to the dried fatty acids the effect of this may be obviated. Silva (*Analyst*, 1898, 77) has noted that Tocher's reagent gives no coloration with these oils, and prefers it for the detection of sesame oil in olive oil.

*Arachis oil* has about the same density as olive oil, but solidifies somewhat less readily. It may often be recognised by its odor and taste, but positively by isolation of arachidic acid. It gives a red color with nitric acid, but yields slowly a solid elaidin with nitrous acid. A sample of so-called "green olive oil, from Malaga," was found by Cailletet to consist solely of arachis oil colored with copper acetate.

*Lard oil* is difficult to detect with certainty in olive oil, but its presence may be inferred from the altered viscosity of the sample, the diminished intensity of the absorption-bands, the higher melting point of the fatty acids, in some cases by the odor of lard developed on warming the sample, and the bromine thermal value.

*Fish oils* will be detected by the smell on warming the sample; by the red color produced on heating the oil with a solution of soda; by the brownish color developed with sulphuric acid, and by the darkening produced on agitating with hydrochloric acid or passing chlorine.

*Hydrocarbon oils* may be detected and determined by the methods described on page 112 *et seq*.

The use of Amagat and Jean's oleo-refractometer may aid in detection of adulteration of olive oil. Oliveri (*J. S. C. I.*, 1894, 45) gives the refraction coefficient of 106 pure olive oils compared with those of other oils, as follows:—

OIL.	DEVIATION
Olive, . . . . .	0 to 2
Cottonseed, . . . . .	.18
Sesame, . . . . .	.15 5
Colza, . . . . .	.26 5
Arachis, . . . . .	.7 5
Castor, . . . . .	.41 to .44

These figures indicate that, by means of the oleo-refractometer, admixtures of any considerable quantity of the above oils with olive oil may be detected, as the refraction coefficient would be above 2. *Arachis*

oil is, however, an exception, since a mixture of 25 per cent. of this and 75 per cent of olive oil with a refraction coefficient of 0.25 would not produce a deviation above 2

OLIVE-KERNEL OIL is of a dark greenish-brown color, and has about the same saponification-equivalent and iodine-absorption as olive oil; but the density is about .920, and it is stated by Valenta to be soluble in an equal measure of glacial acetic acid at the ordinary temperature.

The oils extracted by carbon disulphide from pressed marc ("sulpho-carbon oils") resemble olive-kernel oil in their behavior with acetic acid, usually yield no solid elaidin, have an iodine-absorption of 79 to 80, and are characterized by their dark color and unpleasant smell

TURKEY-RED OIL.—In dyeing cotton turkey-red a necessary stage consists in treating the cloth with oil. The oil employed for this purpose in England is frequently the variety of olive oil known as "Galipoli oil." Although olive oil is not essential, a thoroughly non-drying oil must be used, and this is ascertained by the elaidin-test. A good sample will give a firm and nearly white elaidin. A yellow, soft, or semi-fluid product indicates undesirable admixtures.

Oil suitable for turkey-red dyeing is prepared from somewhat unripe olives, which are steeped for some time in boiling water before being pressed. Through this treatment the oil contains a large proportion of foreign matter, and soon becomes rancid. Another plan is to agitate oil which has been some time in store for several days at a temperature of about 40° C., air being allowed free access. A third method is to add oleic acid to the oil.

Turkey-red oil should form a white emulsion when agitated with a dilute solution of caustic alkali or alkali carbonate. One part of the sample should be beaten up with from thirty to forty parts of semi-normal caustic soda solution. After standing six hours, the mixture should be still homogeneous, without any sign of separation of the oil.

An entirely different preparation, now extensively used as a turkey-red oil, is prepared from castor oil.

### Almond Oil.

*French*—Huile d'amande. *German*—Mandelöl.

(See also p 91) Almond oil is a fixed oil expressed from either sweet or bitter almonds. The oil of commerce is mostly obtained from bitter almonds, the marc of which is then distilled with water to obtain the essential oil. Fixed oil of almonds must not be confounded with

the essential oil of bitter almonds. It is largely employed in the preparation of ointments and emulsions, for which it is better adapted than olive oil.

Almond oil is thin, nearly odorless, of a straw-yellow color and bland taste. It does not solidify till cooled to about  $-20^{\circ}\text{C}$ ., some samples only becoming turbid at that temperature. According to the German Pharmacopeia, almond oil should remain clear when exposed to a temperature of  $-10^{\circ}\text{C}$ . The specific gravity ranges from .914 to .920. It is soluble in 24 parts of cold alcohol or in 6 parts at the boiling point. It consists chiefly of olein, more or less palmitin, and probably its homologues, being also present. It contains no stearin. It readily turns rancid when exposed to the air, but is not a drying oil.

The following are results of the examination of the mixed fatty acids of almond oil —

Solidifying point,	$5^{\circ}\text{C}$	(Hubl)
Titer test (sweet almonds),	9.5-10.1	(Lewkowitsch)
" " (bitter almonds),	11.3-11.8	"
Saponification value (mgrm KHO),	204	(Thoenner)
Iodine value,	93.5-96.5	(De Negri and Fabris.)
Refractive index,	1.4461	(Thoenner)

#### COMMERCIAL ALMOND OIL.

Almond oil is frequently adulterated with, and sometimes entirely substituted by peach-kernel or apricot-kernel oil, which is sold in England as "foreign almond oil." Olive, arachis, sesame, rape, poppy, and lard oils are also liable to be employed.

Many of these additions may be detected by observing the absorption spectrum of the sample, almond oil differing from most vegetable oils in not giving either a banded spectrum or producing strong absorption in the red or violet.

*Cottonseed oil* may be detected by the nitric acid, Becchi's or Halphen's test, or by the solidifying point of the mixed fatty acids (see page 134). Arachis oil may be detected by Renard's test (see "Arachis Oil").

The elaidin-test serves for the detection of poppy and rape oils, the solidification being much retarded by those adulterants. The nitric acid color tests described on page 86 also serve for the detection of several foreign oils. According to the German Pharmacopeia, if 15 parts of the oil be well agitated with a mixture of 3 parts of fuming nitric acid and 2 parts of water, the mixture should be whitish, not brown or red (absence of *cottonseed*, *earlnut* and *sesame* oils), and

after several hours should form a solid white mass (absence of *drying oils*) the aqueous liquid being nearly colorless. The test also detects the presence of peach or apricot oil.

J. D. Bieber recommends that 5 parts of the sample should be agitated with 1 part of a cold mixture of equal weights of strong sulphuric acid, water, and fuming nitric acid. When thus treated almond oil gives a white or yellowish-white liniment, *sesame oil*, a product which is at first green or pale yellowish-red, but changes very rapidly to a dirty orange-red, *peach-kernel oil*, a reddish or peach-blossom color, changing to dark orange. 5 to 10 per cent. of these foreign oils is said to be recognisable.

T. Mahen has determined comparative reactions shown by samples of almond, peach, and apricot oils. A negative reaction with the zinc chloride test suffices to prove the absence of peach and apricot oils.

	ALMOND	PEACH-KERNEL	APRICOT-KERNEL
Specific gravity at 15.5° C. } (=60° F.),	9189	9232	9294
Consistency at -20° C.	{ Opaque and viscid }	Slightly viscid	Slightly viscid
Bromine absorption, Elaidin test, product, . .	White, hard	77 Citron yellow, soft	70 Light yellow, hard
Nitric acid color test, Sulphuric acid color test,	Slight action Yellow to orange	Dark brown Dark brown	Coffee-brown Light brown to red- dish-brown
Zinc chloride color test,	No change	Purple-brown	Muddy brown, with shade of purple

For the nitric acid test 5 c.c. of the sample were shaken vigorously with an equal measure of pure nitric acid of 1.42 specific gravity, and the coloration observed at the end of five minutes, an hour, and five hours.

For the zinc chloride test a saturated solution of zinc oxide in strong hydrochloric acid was prepared. 5 drops of this and 10 of the sample are stirred well together with a glass rod, and the coloration noted.

Pure almond oil gives a homogeneous and very firm mass when shaken with one-ninth of its measure of strong ammonium hydroxide, while the sample is merely clotted in the case of the sample being adulterated with *poppy oil*, the presence of which would be further indicated by the elaidin test, the increased temperature developed with sulphuric acid, and the abnormal iodine-absorption.

*Lard oil* and *olive oil* are indicated by the formation of a white granular deposit when the sample is exposed to a temperature of -5°



C for 20 minutes Lard oil will be further indicated by the odor developed on warming the sample, and by the high melting point of the fatty acids, and olive oil may usually be detected by the banded absorption-spectrum.

An increased saponification-equivalent indicates the presence of *rape oil*

### Arachis Oil. Earthnut Oil. Peanut Oil.

*French*—Huile de pistache de terre *German*—Erdnussöl

(See also p. 91) Earthnut oil is obtained from the nuts of *Arachis hypogaea*, an herb indigenous to America and now cultivated in various countries, the oil being expressed chiefly in France The seeds contain about 45 per cent. of oil, which in India is called *kutchung oil*, and is largely used as a substitute for olive oil

Arachis oil is usually pale greenish-yellow, and of a peculiar nutty flavor and smell, but may be prepared nearly colorless and almost tasteless It becomes turbid at about 3°, and solidifies at about -5° C The specific gravity of the finest quality is .916, and that of the last runnings as high as .920.

Arachis oil contains olein, linolin, palmitin, arachidin, stearin, and probably also lignocerin and hypogein.

Sadtler (*Analyst*, 1897, 284) gives the following analyses of arachis oil from various sources —

	OIL FROM VIRGINIA NUTS	OIL FROM SPANISH NUTS	OIL FROM ALGERIAN NUTS	OIL FROM INDONESIA	COMMERCIAL OIL
Specific gravity at 15° C	0.917	0.9175	0.911	0.920	0.9209
Saponification value, .	192.53	190.68	194.0	193.1	192.1
Saponification equivalent	291.0	294.1	289.0	290.5	292.0
Iodine value, .	91.75	91.17	85.6	95	98.1
Helmert value, . . .	94.87	95.11	..	..	95.86
Reichert-Meißl value,	0.48	1.60	..	..	..
Free acid, as oleic percent	0.55	0.79	0.62	..	6.20
Cold test, .	+ 3° C	+ 3° C	+ 2° C	..	+ 10° C
Mannheim test, .	56.75° C	..	..	49° C.	45.5° C
Melting point of fatty acids, .	29° C	34° C	30° C.	29° C	28° C.
Solidifying point of fatty acids, . . . . .	27.5° C	32.5° C	29° C	25° C	25° C

Arachidic acid presents a close resemblance to stearic acid, but has a higher melting point (75° C.) and is insoluble in somewhat dilute alcohol These characters are utilised for its isolation, and are em-

played in the process for the detection of arachis oil in olive oil described below. Hypogeic acid closely resembles oleic acid, and may be separated from arachidic acid by treating the lead salts with ether.

The following are some results of the examination of the mixed fatty acids of arachis oil.—

Specific gravity at 100° C (water at 15.5° = 1),	0.846-0.8175	
Titer test,	28.1-29.2	(Lewkowitsch)
Melting point,	27.7-34	
Saponification value (mgm of KOH),	201.6	(Thoerner)
Iodine value,	95.5-97	
" " Coronandol nuts,	103.4	(De Negri and Fabris)
Mean molecular weight,	281.8	(Allen)
Refractive index,	1.4461	(Thoerner)

Arachis oil is chiefly employed as an adulterant of and substitute for olive oil. With the elaidin-test it behaves much like olive oil, but gives a reddish coloration with nitric acid, and may likewise be recognised by its taste. It may also be detected and approximately estimated by the isolation of arachidic acid, by a process devised by A. Renard (*Compt. Rend.*, lxxiii. 1330), modified by Lewkowitsch ("Chem. Anal. Oils, Fats and Waxes," p. 445). 10 gm of the sample are saponified, the excess of alkali neutralised with acetic acid, and a solution of lead acetate added. The precipitated lead salts are separated by filtration and extracted with ether, which leaves undissolved the lead palmitate and arachidate. The residue is treated with hydrochloric acid, the acids allowed to solidify, separated from the lead chloride, and dissolved in 50 c.c. of hot 90 per cent. alcohol. If arachis oil was present in the sample, a crop of crystals of arachidic acid will form when the solution cools. The liquid is filtered, and the crystals washed twice with 10 c.c. of 90 per cent. alcohol, and then with spirit of .890 specific gravity, in which they are insoluble. The arachidic acid is next treated on the filter with boiling absolute alcohol, by which it is dissolved, and the resultant solution is evaporated to dryness and the residue weighed. To the amount thus found is added .0025 gm for each 10 c.c. of 90 per cent. alcohol used in the crystallisation and washing of the acid, if the manipulation was conducted at 15° C.; or a correction of .0045 gm per 10 c.c. if at a temperature of 20° C. The fusion point of the arachidic acid

obtained in the above manner is  $71^{\circ}$  to  $72^{\circ}$ , that of the pure substance being  $75.5^{\circ}$ . Rennid obtained from 4.5 to 5.0 per cent. of arachidic acid from arachis oil, and the writer has isolated 5.5 per cent. Hence twenty times the weight of acid found (duly corrected for solubility as already described) will approximately represent the amount of the adulterant in the 10 gm. of the sample employed for the test. The process requires considerable skill to ensure accurate results. It proved unsuccessful with a mixture containing less than 4 per cent of arachis oil, but with one containing 10 per cent of the adulterant the result was within 1 per cent. of the truth.

Jean (*J. S. C. I.*, 1898, 804) proposes a process based upon qualitative tests by Guard and Blarez. Ten gm. of the oil are saponified by being heated at  $110^{\circ}\text{C}$  with a mixture consisting of 3 gm. of potassium hydroxide dissolved in 5 or 4 c.c. of water and 5 c.c. of alcohol at  $36^{\circ}\text{C}$ . The mass is well stirred with a spatula, the heating continued till the soap becomes dry, when it is transferred to a flask and mixed with 100 c.c. of alcohol at  $36^{\circ}\text{C}$ , previously saturated with potassium arachidate at  $11^{\circ}$  to  $12^{\circ}\text{C}$ . The flask is warmed under a reflux condenser until the soap dissolves, and is then left for twelve hours at a temperature of  $15^{\circ}\text{C}$ . The precipitate is filtered off and re-crystallised in the same way from the saturated alcohol. It is then collected, transferred to a flask, and boiled with 50 c.c. of water containing some hydrochloric acid, in order to liberate the arachidic acid. The latter is subsequently extracted with petroleum ether in a separating funnel, and after evaporation of the solvent dried at  $100^{\circ}\text{C}$ . and weighed. Its melting point should not be lower than  $72^{\circ}\text{C}$ .

### Rape Oil. Colza Oil

*French*—Huile de navette    *German*—Rapsöl, Kolsatöl

(See also p 92.) This oil is obtained from the seeds of several species of *Brassica*, of the order *Cruciferae*. The seeds are commonly subjected to steam-heat before pressure, to coagulate the albuminous matter and facilitate the extraction of the oil.

When freshly expressed, rape oil is a yellowish brown or brownish-green viscid liquid, of a peculiar odor and pungent taste, owing to foreign matters present. These impurities separate to some extent by keeping the oil, but cannot be wholly removed by passive treatment. They lessen the combustibility and cause much smoke during the burning. Brown rape oil or sweet rape oil is the commercial name

for the oil as expressed from the seed. It is usually refined by treatment with sulphuric acid, sometimes supplemented by agitation with alkali, and of late years a current of steam has been successfully applied. The refined oil is light yellow and almost odorless.

Some writers distinguish winter from summer rape oil, and both of these from colza oil, but these refinements are nearly obsolete and have but little practical interest<sup>1</sup>

Rape oil stands between drying and non-drying oils. It does not thicken readily when heated and exposed to the air, and yet gives but an imperfectly solid elaidin with nitrous acid. In non-drying characters it is decidedly inferior to olive oil, but superior in its smell and appearance to the lower qualities of the latter. Notwithstanding a slight tendency to gum, it is extensively used for engine and machinery lubrication, as well as for burning in railway and safety lamps.

Rape oil consists chiefly of stearin, olein, and erucin. The presence of other esters—lapin (probably an isomide of olein), behenin, and arachidin—has been affirmed, but can hardly be said to be established. In any case, all the oils from the *Cruciferae* agree in containing esters of high molecular weight, and hence have high saponification-equivalents.

Rape oil and other oils from the *Cruciferae* are commonly stated to contain sulphur compounds, and to give rise to silver sulphide on treating their ethereal solutions with a few drops of solution of silver nitrate in alcohol. If the oil be boiled with a 10 per cent. solution of pure potassium hydroxide, an immersed silver coin becomes blackened. Sulphur is present sometimes, but is accidental. About 1 per cent. of unsaponifiable matter, chiefly phytosterol, is usually present.

<sup>1</sup> By some authorities the term colza oil is restricted to the finest and lightest kinds of oil expressed chiefly from German or East Indian seeds.

The following differences exist between the varieties of rape oil, according to Schübler and Lefebvre —

OIL	SPECIFIC GRAVITY AT 15° C		SOLIDIFYING POINT, °C SCHÜBLER	REMARKS
	Schubler	Lefebvre		
Winter rape	9124	9154	Below 0° -8° to -10°	More viscous than winter rape. Produced largely in France
Summer rapé	9139	9157		
Winter colza	9139	9150	-0°	
Summer colza		9167		

The following are some observed analytic data from mixed fatty acids of rape oil —

Specific gravity at 99° C (water at 15.5° = 1),	8138	(Allen)
100° C (water at 100° = 1),	8758	(Archbutt)
Solidifying point (titer test) (colza oil),	12 7-13 6	(Lewkowitsch)
(rape oil),	11 7-12 2	"
Melting point,	16°-23° C	
Saponification value (mgm KOH),	185	(Thoerner)
Iodine number,	96 3-105 6	
Refractive index,	1.4991.	(Thoerner)

#### ASSAY OF COMMERCIAL RAPE OIL

Rape oil is subject to numerous adulterations, the more important of which can be detected with tolerable certainty.

The specific gravity of the genuine oil averages .915 at 15.5° C. Of 51 samples of genuine rape oil examined by L. Archbutt, 7 gave figures below .9140, 25 between that point and .9150, and 19 between .9150 and .9160. The extreme ranges of variation were .9123 and .9159. Boverton Redwood has communicated to the author the results obtained by careful examination of 30 samples of brown rape oil known to be genuine. The figures range from .9145 to .9154, the average being .9149. The experience of these observers and of the writer himself confirms the results of Archbutt and Redwood, so that .9160 may be regarded as the maximum for genuine rape oil at 15.5° C. North German (Baltic) rape oil is usually somewhat heavier and less pure than the French and Belgian products. The seed crushed in England, imported from the East Indies and all parts of Europe, gives an oil varying in specific gravity from .913 to .917. Black Sea rape oil is usually of inferior quality.

The specific gravity of rape oil is a valuable indication of its purity, as all the ordinary adulterants are heavier than the genuine oil, with the exception of mineral oil, which can be detected and estimated with accuracy by the method described on page 112. Foreign seed oils of more or less drying character, as sesame, sunflower, cress-seed, hemp-seed, cottonseed, or linseed oil, or possibly coconut olein, all range between .920 and .937. Hence, if the sample have a specific gravity of .918, it may possibly contain even 50 per cent. of these oils, while the smell and color will be little affected. Seed and nut oils deteriorate rape oil by increasing its gumming properties, with the exception of arachis oil and coconut olein, and the addition of either of these is improbable. Arachis oil could be detected as in olive oil (page 134), and coconut olein would be indicated by the lowered saponification-equivalent of the sample.

The viscosity of rape oil is a valuable indication of its purity, as it is moderately constant and exceeds that of any oil likely to be used as an adulterant. The sample should always be compared with a specimen of rape oil known to be genuine, or with pure glycerin diluted to 1.226 specific gravity, which at 15.5° C has the same viscosity as average rape oil.

The solubility of genuine rape oil in acetic acid (page 41) is so slight that equal measures of the two liquids are not miscible at 120° C. This peculiar behavior distinguishes the oils from the *Chucifera* from all other fixed oils hitherto examined by the test.

The saponification-equivalent of genuine rape oil averages 324, and ranges from 330 to 318, as an extreme and rarely met with figure. The presence of certain admixtures can therefore be assumed if a still lower figure is obtained. On the other hand, if the saponification-equivalent exceed 330 a *hydrocarbon oil* is probably present, and should be searched for as on page 112. Refined rape oil has been frequently adulterated with purified mineral oil. This addition interferes with the burning qualities of the oil, causing it to smoke and form much deposit on the wick. The unsaponifiable matter naturally present in rape oil was found by B. Redwood to range from 0.18 to 1.00 per cent. Archbutt has occasionally found a somewhat larger proportion.

The iodine absorption of rape oil ranges from 97 to 105 per cent, being slightly less than that of cotton or sesame oil, and considerably below that of the more strongly drying oils.

On exposure to heat in a watch glass at 100° C for several days (see page 68) genuine rape oil slowly thickens and becomes darker, drying gradually at the edges. After continuous heating during four or five days it becomes very viscous, but still remains fluid except at the edges. By comparing in this way, side by side in the water-oven, the sample with a rape oil of known purity, a very useful indication is obtainable. Archbutt found that genuine rape oil exposed in a thin film on a slip of glass, at the ordinary temperature, was still liquid, though viscous, at the end of two years.

The increase of temperature on treating genuine rape oil with strong sulphuric acid averages 59° C, the extreme variations being, according to L. Archbutt, from 55° to 66.7°. Any greater rise than corresponds to that normally yielded by rape oil under the conditions of the experiment may be due to an admixture of cottonseed, hempseed, or linseed oil. If the nature of the admixture can be otherwise ascertained, the proportion of the adulterant can be deduced with

tolerable accuracy from the rise of temperature. Hefner's heat of bromination test will be valuable for the same purpose. Archbutt (*J S C I*, 1897, 311) reports eleven samples of commercial rape oil giving figures from 17.0 to 20.3, the highest being obtained with Black Sea oils.

With the elaidin test rape oil behaves in a peculiar and somewhat characteristic manner. Solidification occurs very slowly, but after 50 to 60 hours the oil is frequently converted into a pasty mass, which is sometimes yellow, and in other cases orange-red or mottled. A separation into a solid and liquid portion frequently occurs. The results are much influenced by the temperature. At 10° C many samples become apparently solid, but on being touched with a glass rod are seen to be a peculiar mixture of solid and liquid. On immersing the bottle containing the product formed at 10° for a short time in water at 15° C., the elaidin forms a thick liquid.

The color tests with sulphuric and nitric acids (pages 85 and 86), and certain other reagents are of value for the detection of certain admixtures, such as linseed and fish oils. Richter states that on shaking 5 c.c. of the sample with 1 c.c. of a solution of soda of 1.34 specific gravity, pure rape oil forms a dirty white milky fluid, *henp oil* a brownish-yellow thick soap; and *train oil* a dark-red solution.

The solidifying and melting points of the fatty acids afford valuable indications in some cases. An admixture of *linseed oil* renders them more fusible, while the acids from *cottonseed oil* have a much higher melting point.

*Fish oils* are recognisable by their taste and odor on warming, and by the colorations developed with sodium hydroxid and sulphuric acid. *Train oil* is said to be best detected by agitating 100 drops of the oil with 1 of sulphuric acid, when the depth of the red coloration will follow the proportion of the adulterant present.

*Cottonseed oil* is one of the commonest adulterants of rape oil. It lowers the saponification-equivalent, raises the melting point of the oil and the derived acids, reduces the viscosity, and increases the specific gravity and the rise of temperature on treatment with sulphuric acid. If refined cottonseed oil, previously deprived of its stearin, has been used as the adulterant, the influence will be less marked.

*Linseed oil* is a common and objectionable adulterant of rape oil, from 10 to 50 per cent. being often added before refining. It is recognisable by the increase in the specific gravity, solubility in acetic acid, drying characters, temperature with sulphuric acid and bromine,

and iodine absorption, and decreased viscosity and saponification-equivalent. The fatty acids are more readily fusible, and the color-reaction with sulphuric acid is modified.

*Hedge-mustard oil* may be used for adulterating rape oil, which it closely resembles. The most characteristic reaction is said to be the production of a green color when the oil is treated with a quantity of alcoholic potash insufficient for complete saponification, and the filtered liquor strongly acidulated with hydrochloric acid.

*Oleic acid* is the only adulterant (except mineral oil and hedge-mustard oil) which could be added to rape oil without tending to increase the specific gravity. The proportion of free (oleic) acid naturally present in rape oil ranges from 0.5 to 5 per cent. Above 5 per cent, may be regarded as due to adulteration. The presence of even a small proportion of free acid has an injurious influence on the burning qualities of rape oil, especially in certain kinds of lamps.

*Free mineral acid* is not unhequently present in rape oil, owing to its imperfect removal during purification. Its presence is highly objectionable in oil intended for lubrication or for greasing steel goods.

### Cottonseed Oil.

*French*—Huile de coton. *German*—Baumwollensamenöl.

(See page 93.) Cottonseed oil is now expressed in enormous quantities in the United States, on the Continent of Europe, and in Great Britain.

CRUDE COTTONSEED OIL has a density ranging from 916 to 930. It contains in solution, often to the extent of 1 per cent., a characteristic coloring matter, which gives it a ruby-red color, sometimes so intense as to appear nearly black. The crude oil gives a bright-red coloration with strong sulphuric acid (page 85). The soap from crude cottonseed oil rapidly oxidises on exposure to air with production of a fine purple or violet-blue coloration.<sup>1</sup> This reaction is characteristic. The coloring matter causes the oil to produce stains, and it is removed by agitating the crude oil at the ordinary temperature with

<sup>1</sup> "Cottonseed blue" is stated by Kuhlmann to have the composition  $C_{27}H_{24}O_4$ . It is amorphous, readily destroyed by oxidising agents, insoluble in water, diluted acids, and alkalis; sparingly soluble in carbon disulphide and chloroform, but more readily in alcohol and ether, and dissolves with purple color in strong sulphuric acid. The unoxidised coloring matter of cottonseed oil has been examined by J. Longmore, who, in a communication to the author, states that it is a pungent golden-yellow product, insoluble in water, but soluble in alcohol and alkaline solutions, and precipitated from the latter on addition of acids. It dyes well and perfectly fast on both wool and silk.



10 to 15 per cent. of solution of caustic soda of 1.06 specific gravity, when the alkali combines with the coloring matter and saponifies a portion of the oil. The mixture becomes filled with black flocks which deposit on standing,<sup>1</sup> and leave the oil but slightly colored. The loss from refining is usually from 4 to 7½ per cent., but occasionally amounts to 12 or 15. Hence it is desirable, before purchasing crude cottonseed oil for refining, to ascertain by a laboratory experiment what the percentage of loss is likely to be. Frequently the treatment with alkali is only carried far enough to remove the greater part of the coloring matter, the oil being then boiled with a solution of bleaching powder and subsequently treated with dilute sulphuric acid. This method of treatment is economical, but the oil acquires an unpleasant taste and smell which cannot be removed.

REFINED COTTONSEED OIL is of a straw- or golden-yellow color, or occasionally nearly colorless. The specific gravity usually ranges from 922 to 926, and the solidifying point from 1° to 10° C. By subjection to cold and pressure a certain proportion of stearin is separated, the melting point of the residual oil being correspondingly lowered. Thus refined oil is usually free from acid, and, when properly prepared, of pleasant taste and adapted for edible and culinary purposes, for which it is now extensively employed, both with and without its nature being acknowledged. It is now substituted for olive oil in some of the preparations of the *United States Pharmacopœia*, but its principal applications are in soapmaking and the manufacture of factitious butter.

It gives but an imperfectly fluid elaidin with mercuric nitrate. The fatty acids obtained from it have a high melting point (38° C.). The color reactions with sulphuric acid and alkali so characteristic of crude cottonseed oil are produced imperfectly or not at all by the refined oil, according to the treatment to which it has been subjected.

Cottonseed oil is not itself very liable to sophistication, but is frequently employed to adulterate other oils. It may be detected by the specific gravity, aided by the color-tests given below and on pages 85 and 86. The results of the elaidin test, with determinations of the iodine-absorption, rise of temperature with sulphuric acid and bromine,

<sup>1</sup> The deposit thus formed, consisting of coloring and albuminous matters, alkali, and partially saponified oil, is technically called "muckage." It is decomposed with a slight excess of acid, and the resulting dark-colored grease is heated to a temperature of 120° C. (250° F.) with concentrated sulphuric acid, which renders insoluble the coloring matters, &c., while the impure fatty acids rise to the surface. On distilling these with superheated steam, a mixture of fatty acids is obtained, which is separated into stearic and oleic acids by pressure. The "cottonseed stearin" thus obtained is employed for making soap and composite candles, and for various adulterations.

and melting point of the fatty acids, enable the proportion of cottonseed oil in a mixture to be approximately determined.

The following are some observed analytic data from mixed fatty acids of cottonseed oil —

Specific gravity at 90° C (water at 15.5° = 1),	8467.	(Allen)
100° C (water at 100° = 1),	8816	(Archbutt)
Solidifying point (titer test),	32.2°-32.7°	(Lewkowitsch.)
	33.3°-34.1°	"
	34.4°-35.2°	"
	35.6°-37.6°	"
Melting point,	35°-40°	"
Saponification value (mgrm KHO),	201.6-208	
Iodine number,	111-115.7	
Refractive index,	1.446	(Thoerner.)

The following are special tests, adapted to the detection of even small quantities of the oil.—

*Silver Nitrate Test.*—Becchi has proposed the use of silver nitrate for the detection of cottonseed oil. The method has been found very useful, and several modifications of the test are in use. It may be applied to the oil or the mixed fatty acids therefrom, but is not applicable to oil that has been heated to 245° C. According to Del Torre the following reagents are required:—

I	
Silver nitrate, . . . . .	1.0 grm.
Alcohol, 98 per cent (by vol), . . . . .	200.0 c.c.
Ether, . . . . .	40.0 c.c.
Nitric acid, . . . . .	0.1 grm.
II	
Pentylalcohol, . . . . .	100.0 c.c.
Rapeseed oil, . . . . .	15.0 c.c.

Ten c.c. of the oil to be examined are mixed in a test-tube with 1 c.c. of reagent I, and then shaken with 10 c.c. of reagent II. The mixture is next divided into two equal portions, one of which is immersed in boiling water for fifteen minutes. The heated sample is then removed from the water-bath, and its color compared with the unheated half. Presence of cottonseed oil is indicated by the reddish-brown coloration of the heated portion. Only the purest alcohol should be used, and the rape oil used should be "cold drawn," and only slightly colored, it should be filtered in a hot-water oven before preparing the reagent. To guard against errors from impurity of the reagents, a blank test should be instituted side by side with the actual test.

The part played by the rape oil in this test is explained, according to Becchi, by the fact that whereas fresh cottonseed oils give the silver nitrate reaction without rape oil, old and rancid samples or their mixed fatty acids do not react unless this oil be added. Many chemists consider the addition of rape oil unnecessary. Pearmain and Moor state that by the following procedure as little as one per cent. of cottonseed oil may be detected. The reagent is prepared as follows: 1 gram of finely powdered nitrate of silver is dissolved in 100 c.c. of 95 per cent. alcohol; when dissolved, 20 c.c. of ether and one drop of nitric acid are added; 2 c.c. of this reagent is well shaken with 10 c.c. of the oil to be examined, and placed in boiling water for ten minutes. Any blackening due to reduced silver proves the presence of cottonseed oil.

*Nitric Acid Test*—On shaking cottonseed oil with nitric acid of 1.37 or 1.38 specific gravity, a rich brown coloration is produced. Some writers have advocated the use of a stronger acid, but Lewkowsitch states that acid of 1.375 specific gravity gives the most definite results. The coloration is equally distinct in the case of oils which have been heated to 240° C., and in this respect the test is superior to Becchi's test. Occasionally samples of American cottonseed oil are encountered which react so faintly with nitric acid as to make it impossible to detect adulteration by them to the extent of 10 per cent.

*Hulphen's Test* (*Analyst*, 1897, 326)—Carbon disulphide, containing about one per cent of sulphur in solution, is mixed with an equal volume of pentyl alcohol. Equal volumes of this reagent and the sample—about 3 c.c. of each—are mixed and heated in a bath of boiling brine for fifteen minutes. If no red or orange tint is produced, 1 c.c. of the reagent is added, and if after five or ten minutes' more heating no color is shown, a third addition of 1 c.c. may be made. It is stated that the depth of color is not the same with all samples. It is possible to detect very small quantities of cottonseed oil by this test. Lard and lard oil derived from animals fed on cottonseed meal will often give a faint reaction. The acids derived from cottonseed oil also give the reaction distinctly. Oil heated briefly to 245° C. still gives the reaction, but with diminished intensity.

COTTONSEED STEARIN is, properly speaking, the solid fat separated from cottonseed oil by cooling and pressing. A product so obtained is stated to be employed for the manufacture of butter substitutes, and to have nearly the same specific gravity as butter-fat. The article known in commerce as "cottonseed stearin" is usually impure stearic acid from cottonseed oil, obtained by the method given in the footnote on page 141. The crude oil expressed from decorticated cottonseed

is sometimes very rancid and semi-solid at the ordinary temperature from the separation of solid fatty acids in the free state. By pressure it would yield a product similar to that obtained by distillation.

#### Maize Oil (Corn Oil, U. S. A.).

*French*—Huile de maïs. *German*—Maisöl.

(See also p. 93.) Maize oil is obtained from the seeds of the *Zea Mays*, either by expression or from the residue of the fermentation vats after they have been used for the preparation of alcohol. The latter product is much darker in color and apt to contain more free acid.

According to J. C. Smith (*J. S. C. I.*, 1892, 504), maize oil is practically without drying power, even when boiled or after the addition of litharge. On passing a current of air through it for an hour at a temperature of about 150° C., the oil becomes slightly darker in color and rather more viscous, but not to the same extent as cottonseed oil. If to the oil so treated a small quantity of manganese borate be added, the mass acquires siccative properties to a slight extent, and a thin film on lead dries in from ten to twenty hours, but not completely. Like cottonseed oil, the elaidin reaction gives rise to a mass having a buttery consistency. The oil dissolves readily in acetone, and more sparingly in alcohol or glacial acetic acid.

Maize oil is used for lubricating, burning, and soap-making. It has also been proposed as a substitute for olive oil, and has been employed to adulterate lard.

The following figures are compiled from various sources:—

Specific gravity at 15°50,	910–924.
Solidifying point,	–10 to –20.
Saponification equivalent,	290–298
Iodine-absorption,	111–122.
Acetyl value,	7.8–8.75. (Lewkowitsch)
Heat of bromination,	21.5 (Hegner and Mitchell)
Solidifying point of mixed fatty acids, 14°–16°.	(DeNegri and Fabris)
Melting " " "	18°–20° " "
Iodine number,	113–115 " "

J. C. Smith obtained from 100 grm. of oil volatile acids sufficient to neutralise 0.56 grm. KOH. This would probably correspond to a Reichert number between 2 and 3.

**Sesame Oil. Teel Oil. Gingili Oil.***French*—Huile de sésame. *German*—Sesamol

(See also p. 93.) Sesame oil, sometimes called benne oil, though distinct from the oil of *ben* or *behen*, has a yellow color, usually of a deeper hue than almond oil, is thinner than most oils, nearly odorless, and has a bland and agreeable taste. That expressed from the seeds congeals at about  $-5^{\circ}$ , but that extracted by solvents at about  $+5^{\circ}$  C.

Sesame oil consists of olein, with palmitin, stearin, and linolin. A small quantity of a peculiar, probably resinous, substance may be extracted from the oil by agitation with alcohol or glacial acetic acid. The acetic solution has a blue color, changing to greenish-yellow, on addition of a cold mixture of equal weights of sulphuric and nitric acids. It is dextro-rotatory, and in the absence of castor, croton, and resin oils this property may serve for its detection. It is an imperfectly drying oil, and does not readily turn rancid. Concentrated sulphuric acid converts it into a brownish-red, gelatinous mass. "German sesame oil" is a name sometimes given to camelina oil. The compulsory addition of 10 per cent of sesame oil to butter substitutes has been adopted in Germany to facilitate detection of butter adulteration.

The mixed fatty acids from sesame oil have given the following figures.—

Solidifying point (titer test),	21.2°-22.9°	(Iewkowsitch)
	22.9°-23.5°	"
	23.7°-23.8°	"
Melting point,	21°-31.5°	
Saponification value (mgm. KHO),	199.3-201.6	
Iodine absorption,	109-112	
Refractive index,	1.161	(Thoerner)

Sesame oil may be detected by a reaction with furfural, as proposed by Villavecchia and Fabris, being a modification of a test originally proposed by Baudouin. The reagent is 0.1 c.c. of a 2 per cent alcoholic solution of furfural mixed with 10 c.c. of hydrochloric acid. Instead of mixing this directly with the oil, Wauters suggests that the sample to be tested should be poured upon the reagent. Less than 1 per cent of sesame oil will produce a crimson color at the point of contact. If the sample used be rancid, a brownish tint may be produced, which will mask the reaction when only small amounts of sesame oil are present.

Tocher detects the presence of sesame oil as follows 15 c.c. of the oil are shaken in a separating bulb with a solution of 1 gram of pyrogallol in 15 c.c. of concentrated hydrochloric acid. The aqueous liquid is drawn off and boiled for about five minutes, in the presence of sesame oil it becomes colored, appearing red by transmitted and blue by reflected light

*Rape oil* may be detected by saponification value, specific gravity, and solidifying and melting points of the fatty acids

*Poppyseed oil* may be detected by the iodine number and thermal tests

*Cottonseed oil* may be detected by Halphen's and Lavache's tests and the melting point of the mixed fatty acids.

*Arachis oil* will be indicated by lower specific gravity and presence of arachidic acid

### Linseed Oil.

*French*—Huile de lin    *German*—Leinol, Leinsamenöl.

(See also p. 93) Linseed oil is the oil expressed from the seeds of *Linum usitatissimum*, or flax-plant

Flax is commonly grown in India as a mixed crop with mustard and rape, and hence the oil from Indian linseed is never perfectly pure. In Black Sea ports it is the practice to add 1 measure of hemp to every 19 of linseed, and adulteration is also conducted in much more considerable proportions. The varieties of linseed oil recognised in commerce are raw, refined, artist's, and boiled oil. It is usually refined by agitating the raw oil in lead-lined tanks with about 1 per cent. of concentrated sulphuric acid (specific gravity 1.845), and washing the product by boiling it with water, with or without open steam. After settling, the water and foots are run off from the refined oil.<sup>1</sup> Boiled oil is described on page 149

Freshly expressed linseed oil is a brownish or yellow liquid. The oil obtained from the seeds by cold pressure has a golden yellow color and a peculiar bland taste; that obtained by hot pressure varies in

<sup>1</sup> To prepare artist's oil, raw oil is allowed to stand for weeks or even months to cause impurities to settle, and then treated with litharge or lead acetate. It is then bleached by exposure to sunlight. Various secret methods of treatment are employed. Iron or zinc sulphate is sometimes used, and is said to hasten the deposition of impurities. The lead is often separated by sulphuric acid, which forms lead sulphate, which carries down impurities. Lavache treats the oil with metallic lead and removes the lead which passes into solution by means of a solution of zinc sulphate, whereby lead sulphate is precipitated and an oxide of the other metal remains in solution.

color from amber-yellow to yellowish brown, has a more or less acrid taste, and possesses a stronger odor than the cold-pressed oil. The specific gravity of the pure oil is generally about 935, but may vary from 931 to 937. It becomes thicker when cooled, and solidifies at about  $-27^{\circ}\text{C}$  to a yellowish mass. It imparts a yellow color to alcohol when agitated with it, and dissolves in about 40 measures at the ordinary temperature or in 4 or 5 at the boiling point of the spirit. It produces great heat when treated with concentrated sulphuric acid or bromine, and is inflamed by fuming nitric acid. It does not yield a solid product under the influence of nitrous acid.

Linseed oil is the most important of the class of drying oils. Its applications in the arts, as in the manufacture of paint, varnish, oil-cloth, and printing ink, are all based on its property of drying on exposure, a character which is more fully considered later. In consequence of this tendency to combine with oxygen, it evolves much heat when exposed to the air in a finely divided condition, sometimes sufficient to cause the inflammation of cotton-waste or similar material saturated with the oil.

Linseed oil contains stearin, palmitin, and myristin, which together form about 10 to 15 per cent. The remaining portion consists of isoholenin with smaller proportions of linolin, hnoleum, and olein. The proportion of unsaponifiable matter is a little over 1 per cent.

LINOLIC ACID was isolated by Schuler in the following manner:—Linseed oil was saponified with solution of caustic soda, and the soap purified by repeatedly salting out. The aqueous solution of the soap was then precipitated by calcium chloride. From the well-washed precipitate the calcium linolate was dissolved out by ether. The ethereal solution was decomposed by agitation with cold hydrochloric acid, the ethereal layer separated and distilled at as low a temperature as possible in a current of hydrogen. The residual acid had a dark-yellow color, and was further purified by dissolving it in alcohol, saturating the solution with ammonia, and then precipitating with barium chloride. The barium linolate thus obtained was washed, pressed, and repeatedly recrystallised from ether, and then converted into the acid by a treatment corresponding to that described for the calcium salt. The acid was dried in a vacuum over sulphuric acid and a mixture of ferrous sulphate and lime.

Linolic acid is a thin oily liquid, of faint yellow color. It remains liquid at  $-18^{\circ}\text{C}$ , and at  $14^{\circ}\text{C}$ . has a density of 9206. It is said to possess a faintly acid reaction, and to have a taste which is at first pleasant and afterwards harsh. Linolic acid does not form a solid

product on treatment with nitrous acid. With nitric acid it swells up considerably and yields suberic acid,  $C_8H_{14}O_4$ , a little oxalic acid, and a greasy resin.

On exposure to air linolic acid absorbs oxygen, becoming thick and ultimately so viscid as scarcely to flow, but remains unchanged in color. When spread in a thin layer on wood and exposed to the air, linolic acid forms a varnish, but on glass only becomes tough. The product is said to have the composition of a hydrate of oxylinolic acid,  $C_{18}H_{32}O_5 \cdot H_2O$ . When heated to  $100^\circ$  this gives off 6.7 per cent. of water and becomes blood-red. By prolonged contact with air, and more quickly if frequently moistened with ether, colorless oxylinolic acid loses its viscid consistence, and is converted into a body called linoxyn. It is a neutral, amorphous, highly elastic mass, resembling caoutchouc, heavier than water, and insoluble in it and in dilute acids, alcohol, or ether, but swells up and dissolves in a mixture of alcohol and chloroform. In warm solution of caustic potash, and more slowly in ammonia, it dissolves to a red liquid, which, when supersaturated with an acid, yields a yellowish-red, flocculent precipitate, soluble in alcohol, and still more in ether, exhibiting the composition and properties of oxylinolic acid.

**LINOLATES.**—The salts of linolic acid are difficult to obtain pure. They are white, mostly uncrystallisable, become colored on exposure to air, and are soluble in alcohol and ether. Potassium and sodium linolates containing an excess of alkali absorb oxygen greedily and become yellow and dry when exposed in a finely divided state to the air, dissolve in water with dark brownish red color, and give, on addition of hydrochloric acid, a brown greasy resin. The ethereal solution of lead linolate, when evaporated on a glass plate, leaves a white amorphous residue of lead oxylinolate. The acid separated from this salt by hydrogen sulphide and dissolved in alcohol remains on evaporation as a nearly colorless viscid mass, which becomes blood-red without change of composition when heated to  $100^\circ$  or treated with acids or alkalis. The colorless alcoholic solution of oxylinolic acid is not altered by alkali carbonates at the boiling heat, but caustic alkalis turn it red even at ordinary temperatures.



The mixed fatty acids from linseed oil have furnished the following figures —

Specific gravity at 15.5° C ,	0233.	(Allen )
Specific gravity at 99° (water at 15.5° = 1),	8612	(Allen.)
Specific gravity at 100° (water at 100° = 1),	8925	(Archbutt )
Solidifying point (titer test),	$\begin{cases} 19.0^{\circ}-19.4^{\circ} \\ 20.2^{\circ}-20.6^{\circ} \\ 17.5^{\circ} \end{cases}$	$\begin{cases} \text{(Lewkowitsch )} \\ \text{''} \\ \text{(Allen )} \end{cases}$
Saponification value (mgrm KOH),	196-199	
Iodine absorption,	160-182	
Refractive index,	1.4546	(Thoenes )

**OXIDATION OF LINSEED OIL.**—The most valuable property of linseed oil is that of taking up oxygen and becoming converted into a tough or hard varnish. This tendency is much enhanced by heating the oil above 130° C. while passing a current of air through or over it, and subsequently increasing the temperature until the oil begins to effervesce from evolution of products of decomposition. The product is called "boiled oil." By continued boiling the oil becomes very thick and may be drawn out into elastic threads, which are very sticky but do not produce a greasy stain on paper. This product is used in the manufacture of printing ink.

The chemical changes which occur in the boiling and drying of linseed oil are very imperfectly understood. According to Mulder, part of the linolin is decomposed during the boiling, with formation of linolic anhydride, or a more highly oxidized body such as hydroxylinoic acid. According to W. Fox, the oxidation products are formed from the acids, and the glycerol breaks up into acids of the acrylic series, forming the irritating vapors which always accompany oil-boiling. Acetic and formic acids are prominent constituents of these vapors, and carbon dioxide and water are also present. The statements of Mulder and Fox are probably too sweeping. The author isolated 8.8 per cent of nearly pure glycerol from the products of the saponification of linseed oil which had been boiled by the steam process. Bauer and Hazura (*Monatsh. Chem.*, ix 459) also consider Mulder's explanation of the drying of linseed oil to be only partially correct. The subject has been reinvestigated by these chemists, who arrived at the following conclusions.—

1. The more linolenic acid an oil contains the more rapidly it dries.

2 The products of oxidation are not merely additive compounds, but contain part of their oxygen as OH groups. The oxidation of the salts is similar to that of the acids themselves.

3 By very prolonged exposure to air at ordinary temperatures, or by shorter exposure at about 80° C, the fatty acids are fully oxidised with formation of a resinous sticky solid, insoluble in ether, but reconverted into acids soluble in ether on heating with alkali.

4. The drying properties of oils depend upon the presence of linolic, linoleic, and isolinoleic acids, as oleic acid forms no solid oxidation products. During the drying of linseed oil only the tritenyl of the non-drying esters is oxidised, as is shown by the very small quantities of carbonic, formic, and acetic acids formed by passing pure air through pumice soaked in linseed oil. The samples of linseed oil which were still in the first stage of oxidation, as shown by their being still soluble in ether, contained 8.9 and 12.1 per cent of free acid. The body insoluble in ether, called by Mulder *linoxyn*, produced by the oxidation of linseed oil, is an ester termed *hydroxylinolin*.

By adding litharge, red-lead, ferric oxide, or manganese dioxide or hydride during the process of boiling, the oxidation and consequent drying of the product are still further facilitated. The nature, proportion, and mode of adding these substances are usually kept secret. Lead acetate and manganous borate are among the most approved. The action of some at least of these "driers" (e.g., compounds of manganese) seems to be that of carriers of oxygen, while litharge dissolves in the oil and acts partly as a carrier of oxygen and partly as the base of certain salts which oxidise very rapidly.

The solid siccatives formerly in use have been lately replaced by soluble compounds. These possess the advantage that they may be incorporated with the oil at a lower temperature or even in the cold if the siccative has been previously dissolved in turpentine. Compounds containing lead alone are but little used, the ordinary preparations being manganese resinate, lead and manganese resin ate, manganese linolate and lead and manganese linolate (i.e., preparations obtained from the mixed linseed oil acids). Products obtained with other metals, such as copper and zinc, have been found to be useless. The resinates are made either by melting together the resin, usually colophony, with the metallic oxide, or by precipitation of the resin and precipitation from the aqueous solution of the soap by means of a salt of manganese or lead.

To be effective the siccative should be completely soluble, any suspended oxide being not only useless but harmful. The solvents employed in testing the preparation are ether and (in the case of lead resinate) chloroform. When insoluble in these the sample will be insoluble also in moderately hot linseed oil, and therefore worthless. From the examination of a large number of samples, Weger (*Analyst*, 1896, 300) finds that the soluble manganese in fused

resinates seldom exceeds 2.3 per cent, but in precipitated resinates it may reach 6 or even 7 per cent. Good preparations of fused manganese binoxide have 9 and in some cases even 11 per cent. The preparation most used is fused lead and manganese resinate, the most suitable proportion of lead to manganese appears to be 5:1.

The quantities required for the preparation of a good varnish are: Melted manganese or lead-manganese resinate, 2 to 3 per cent, melted manganese binoxide, 1 per cent, and precipitated manganese resinate, 1 to 1.5 per cent.

For the analytical examination, Weger burns off the organic matter and determines the manganese and lead in the ash. It is useless to weigh the total ash, since resinates often contain sand. If, after the removal of the lead, calcium is present to any extent, the manganese and calcium are determined together in neutral solution as carbonates, the manganese titrated and the calcium determined by difference. The insoluble lead and manganese are determined by dissolving a fresh portion of the sieve-residue in ether or chloroform, filtering, washing, igniting, etc. The soluble manganese is determined by the difference between this result and that of the total manganese, and the result may be controlled by determining the soluble manganese in an aliquot portion of the filtrate. The soluble lead must be determined by difference, since the chloroform cannot be completely evaporated from the resinatic solution, traces remaining except at a red heat when most of the lead volatilizes with it as lead chloride.

The change of composition undergone by 100 grm. of linseed and poppy oils by exposure to air during 18 months was found by Cloez to be as follows:—

	LINSEED OIL			POPPY OIL		
	C	H	O	C	H	O
Composition of original oil,						
Composition after 18 months,	77.57	11.33	11.10	77.50	11.10	11.10
Difference,	72.27	10.57	24.16	71.38	10.64	25.08
	-5.30	-0.76	+13.06	-6.12	-0.76	+13.98

The quantity of oxygen absorbed was greater than that given off in the form of carbon dioxide and water, and the oil finally showed a considerable increase in weight. The action of light is not essential, but was found to facilitate the change, the more refrangible rays having the greatest influence. In the dark the chemical change is induced very slowly, but when once begun it proceeds rapidly.<sup>1</sup>

<sup>1</sup> According to Mr. T. Duggan, to whom the writer is indebted for numerous specimens and much valuable information on linseed oil and allied subjects, the oil thickens in the dark, but loses its drying power in some measure, requiring it on subsequent exposure to light and air.

When a drying oil containing manganese oxide in solution is dissolved in an equal measure of benzene and agitated with air in a closed vessel, rapid absorption of oxygen takes place, especially at a temperature of 40° to 50° C. If the supply of air be repeatedly renewed the liquid becomes thick, and on distilling off the solvent a residue is obtained which solidifies on cooling to a dry and perfectly elastic solid. By limiting the oxidation various intermediate products are obtainable. The last product is characterised by its elasticity and its insolubility in water, alcohol, and ether. It is almost instantly saponified by caustic potash in the cold; and on subsequent separation of the fatty acids it is found that the solid acids have undergone no alteration, whilst the liquid fatty acid has been converted into viscous products, characterised by their solubility in water and by the salts which they form.

#### ASSAY OF GENUINE LINSEED OIL.

Linseed oil is often sophisticated, but even when perfectly genuine its quality varies within wide limits. In practice, the best oil is that which dries most perfectly, but the rapidity of drying and the consistency of the ultimate product are most important factors in judging of the quality of linseed oil. Thus the dried oil may be tough, very elastic, hard and brittle, or rotten. An oil giving a hard product is to be preferred, as elasticity can be readily imparted in the after-treatment if required.

Raw oil, intended for making pale boiled oil or varnish, should not have a specific gravity much below 935, or it will be apt to contain a notable proportion of other seed oils; 3 per cent. of such admixtures is the maximum allowable in linseed to be used for producing this class of oil.

Among the various methods of judging of the quality of linseed oil, those proposed by Livache and Bishop (see page 69) are the most satisfactory.

The iodine-absorption of an oil appears to increase with its drying powers, and the determination could probably be employed with advantage for ascertaining the quality of linseed oil.

The temperature-reaction with sulphuric acid appears to vary somewhat with the character of a linseed oil. Thus J Baynes (see footnote on page 77) has communicated the following figures to the author:—

	TIME OF TEMPERATURE, °C
Baltic linseed oil, two years old, extra good for varnish,	121
Another similar sample,	123
Old sample, from English seed,	115
Russian oil, . . . . .	113
La Plati oil,	112
Fresh oil, from East Indian seed,	104

The nature of the *driers* added to linseed oil can be generally inferred from an examination of the *ash* left on burning 100 grm of the sample, a little at a time, in a porcelain dish. The residue should be specially tested for lead, copper, zinc, iron, manganese, and borates, Sulphates, acetates, borates, and most other salts may be detected by agitating the original oil with a solution of sodium carbonate, separating the aqueous portion, and examining it for salt-radicals in the usual way.

#### DETECTION OF ADULTERATIONS OF LINSEED OIL

Linseed oil is liable to be adulterated in a variety of ways. Cottonseed, nigerseed, and fish oils are added, mineral and rosin oils, often both together, are largely used, and rosin itself is also added.

The drying and oxygen absorption tests described above are valuable as indications of quality, and hence probable adulteration, but it must be borne in mind that samples of genuine linseed oil differ much in their behavior under these tests.

The specific gravity of genuine raw linseed oil lies between 931 and 937, that of the boiled oil between 939 and 950. *Mineral* and all foreign *seed oils* are lighter than linseed oil, while *rosin* and *rosin oil* are much heavier. By the judicious use of a suitable mixture of mineral and rosin oils, extensive adulteration can be effected without alteration of the specific gravity.

The solidifying point of pure raw linseed oil is about  $-27^{\circ}\text{C}$ , but samples containing other *seed oils* solidify at a higher temperature. The same remark applies to the relative fusibility of the fatty acids, those prepared from cottonseed oil having an exceptionally high melting point.

The iodine-absorption is a valuable method of determining the proportion of a *seed oil* in linseed oil, provided other adulterants are absent. Fresh raw linseed oil assimilates over 170 per cent of iodine, while *cottonseed oil* takes up only 102 to 111 per cent. Some fish oils absorb as much iodine as does linseed oil.

The rise of temperature on treating the oil with strong sulphuric

acid (pages 76 and 153) is also a useful test for linseed oil, which gives more heat than any other *seed oil*, though it is equalled and even exceeded in this respect by some of the *fish oils*.

Hehner's heat of bromination test (page 80) is also of value. Archbutt (*J. S. C. I.*, 1897, 309), as the result of the examination of ten samples of raw linseed oil, gives bromine thermal values ranging from 28.5 to 32.5.

The sulphuric acid color-test described on page 85 is a useful indication of the purity of linseed oil. With a genuine sample a dark-brown clot is formed, if *rosin oil* or *fish oil* be present a reddish-brown spot quickly forms, which in the former case retains its red tint for a long time, whilst a peculiar scum forms over it. This test is also applicable to the detection of rosin oil in *boiled* linseed oil.

*Fish oils* may also be detected by the darkening produced by passing a rapid stream of chlorine through the oil, and by the reddish color produced by boiling the oil with alcoholic soda. They are further recognizable by the taste and the smell of the sample on warming, and by the peculiar scum which rises when such oil is heated to boiling. As a test for *cod oil*, which is not unfrequently used in the case of linseed oil intended for the preparation of printing ink, A. Morell recommends the following test.—10 grm. of the oil are well agitated with 3 grm. of common nitric acid, and the whole left to stand. With pure linseed oil the color will change during the stirring to sea-green, afterwards becoming dirty greenish-yellow, whilst the acid assumes a light yellow color. In presence of even 5 per cent of cod oil, after standing some time the oil is said to acquire a dark brown color, while the acid is tinged orange or dark yellow, according to the proportion of the adulterant present. A similar test has been described by A. Conrath for the detection of *rosin oil*.

*Japanwood oil* (page 95) is distinguished by the very hard black clot it gives with sulphuric acid, and by yielding a highly colored semi-solid product with the elaidin test. If heated for a short time to about 300° C., the oil becomes a transparent jelly, the change occurring either at once or on cooling.

*Hydrocarbons* are largely employed for adulterating linseed oil. They may be determined with accuracy as described on page 112. A mixture of *mineral* and *rosin oil* is frequently used, *rosin* itself being sometimes also added. The mineral oil is usually of low density (865 to 880), as the heavier oils are of too greasy a nature. The rosin oil employed for adulterating linseed oil is free from smell even when heated, but has a peculiar taste which is not masked by the linseed

oil. The presence of rosin oil causes linseed oil to remain "tacky" for a long time, and prevents it ever becoming hard.

The analysis of a sample of boiled linseed oil which, in addition to containing various mineral additions and free fatty acids, is also adulterated with rosin, rosin oil, and mineral oil, is a complex problem. The following plan is recommended, the substantial accuracy of the results yielded has been established in the author's laboratory. 25 gm. of the sample should be shaken in a separator several times with dilute hydrochloric acid. The aqueous liquid, which may contain lead, zinc, manganese, borates, and other *mineral additions*, is separated from the oily layer, and the latter is washed by agitation with water till the washings no longer reddin litmus. The oil is then treated with rectified spirit, and the free fatty and rosin acids titrated with standard alkali and phenolphthalein as described on page 105. The neutral point having been reached, the alcoholic layer is separated from the residual oil, which consists of *neutral fatty oil* and *hydrocarbon oils* of the original sample. These may be separated as described on page 112. The alcoholic solution is then concentrated, water added, and any globules of oil dissolved by agitating with petroleum spirit. After separation from the aqueous liquid and evaporation of the solvent, the small residue of neutral oils may be weighed, and the amount found added to the main portion. The aqueous solution is then acidulated with dilute hydrochloric or sulphuric acid, when an oily layer is obtained, consisting of the free fatty and rosin acids of the original sample, together with such additional amount as may have been formed by the decomposition of metallic soaps in the first stage of the process. This is separated from the aqueous liquid, washed with a little water, and filtered through wet paper. On subsequently drying the filter in the water oven, the fatty acids pass through, and can be collected in a small tared beaker, the portion remaining on the filter being dissolved in ether, and treated as described on page 51. After weighing the fatty acids in the beaker, 1 gm. is treated by Twitchell's process for the separation of fatty and rosin acids. The amount of *resin* thus found, subtracted from the mixed fatty and rosin acids, gives that of the *fatty acids* alone. By agitating the original sample with alcohol, separating the spirituous solution from the undissolved oil, and titrating the former with standard alkali, the sum of the fatty and rosin acids originally existing in the oil can be ascertained.

### Castor Oil

French—Huile de ricin German—Ricinusöl

(See also p 95) Castor oil is expressed from the seeds of *Ricinus communis*, of which it constitutes nearly half the weight. If not perfectly clear, the oil is filtered, or treated with a small proportion of magnesia and animal charcoal.

Castor oil is a transparent, colorless, or pale greenish-yellow liquid, having a faint odor and disagreeable taste. At a low temperature it thickens and deposits white granules, and at or about  $-18^{\circ}\text{C}$  it solidifies to a yellowish mass.

Castor oil is distinguished in its physical characters from most other fixed oils by its high specific gravity and viscosity, ready solubility in alcohol and insolubility in petroleum spirit. These characters are of value for the assay of commercial samples, and are described below. Some samples of castor oil are optically active. Deering and Redwood have observed a rotation in Indian castor oils, of from  $+7.6^{\circ}$  to  $+9.7^{\circ}$ . The observations were made with a Hoffmann Laurent polarimeter.

Castor oil contains ricinolin and isoricinolins, dihydroxystearin, and a small quantity of stearin. Palmitin and olein are absent<sup>1</sup>.

RICINOLIC ACID,  $\text{HC}_{18}\text{H}_{33}\text{O}_4$ , may be prepared from castor oil by the method employed for the preparation of oleic acid from oils, or castor oil may be saponified, and the soap fractionally precipitated with calcium chloride. The first third should be rejected. The later fractions are purified by crystallisation from alcohol, and decomposed by dilute hydrochloric acid.

Ricinolic acid is a thick oily liquid, which solidifies below  $0^{\circ}$ . It is insoluble in water, but is miscible in all proportions with alcohol and ether. The alcoholic solution has an acid reaction, an unpleasant, persistent, acid taste, and does not oxidise in the air. Like oleic acid, it combines with  $\text{Br}_2$ , and by treatment with nitrous acid is gradually converted into a stereo-isomer, ricinelaidic acid, a body crystallising from alcohol in white needles, melting at  $50^{\circ}\text{C}$ , and forming an additive compound with  $\text{Br}_2$ . When heated with phosphorus, iodine, and water, ricinolic acid yields an iodo-acid, which by

<sup>1</sup> C. R. A. Wright finds that the mixed acids from castor oil have a mean combining weight ranging from 293 to 299, that of ricinolic acid being 298. A sample of castor oil, analysed very carefully in the writer's laboratory, gave 9.13 per cent of glycerol and 96.17 per cent of acids, of 306.5 mean combining weight and 9509 specific gravity at  $15.5^{\circ}\text{C}$ .



the action of nascent hydrogen (hydrochloric acid and zinc) is converted into stearic acid

When distilled in a partial vacuum, ricinolic acid yields enanthal or normal heptonic aldehyde,  $C_6H_{13}COH$ , and an acid of the acrylic series. The reaction may be used for the detection of castor oil. For this purpose the sample should be saponified, and the fatty acids liberated and rapidly distilled in a small retort. The distillate is shaken with a saturated solution of acid sodium sulphite, the resultant crystals pressed, dissolved in a solution of sodium carbonate, and the liquid distilled in a current of steam. The enanthal will collect on the surface of the distillate as a highly refractive liquid, of peculiar aromatic odor, boiling at  $154^\circ$ . Enanthal is also produced by subjecting the alkali-metal salts of ricinolic acid to dry distillation, but if caustic soda be present in addition, sodium sebate is formed, and methyl-hexyl carbinol and methyl-hexyl ketone are found in the distillate.

Ricinolic acid forms a series of salts, many of which are soluble in, and may be crystallised from, alcohol or ether.

The following are the results of examination of the mixed fatty acids of castor oil —

Specific gravity at $15.5^\circ C$ ,	9509	(Allen)
" " " $93^\circ-99^\circ$ ,	8960	"
Solidifying point,	$3^\circ$	(Häbl)
Melting point,	$1^\circ$	"
Iodine value (per cent),	87-94	
Refractive index,	1.4516.	(Thoerner)

#### COMMERCIAL CASTOR OIL.

The peculiar physical characters of pure castor oil distinguish it sharply from most other oils, but it is liable to adulterations, which, when not in excessive proportion, are difficult to detect. The most probable adulterants are poppy oil, lard oil, coconut oil, seal oil, rosin oil, and the oxidised or "blown" oil now manufactured from rape, linseed, or cottonseed oil.

The specific gravity of the pure oil is exceptionally high. It usually ranges between 960 and 964, and any sample showing less than 958 is open to suspicion. The only other commercial fixed oil having as high a specific gravity as castor oil is *blown oil*. *Rosin oil* has often as high a specific gravity as 998, but it can be detected and determined with accuracy as described on page 112. The viscosity of castor oil

at the ordinary temperature exceeds that of all other natural fixed oils, but is approached by rosin oil and blown oil.

The solubility of castor oil in alcohol is much greater than that of any oil likely to be used as an adulterant. According to the *British Pharmacopoeia*, it is entirely soluble in an equal measure of absolute alcohol, and in twice its measure of rectified spirit. This description is faulty, at a temperature of 30° C. it is strictly correct, provided the strength (specific gravity 838) and volume of rectified spirit and temperature prescribed be rigidly adhered to, but the use of a slightly weaker spirit, the addition of a very trifling proportion of water, or a slight reduction of temperature, causes the castor oil to be thrown out of solution. It is perhaps preferable to use 4 measures of rectified spirit at 15° C. than half that proportion at the higher temperature. If any considerable proportion of adulterant be present, the liquid separates on standing into three layers, of which the lowest is usually the foreign oil, and its volume will afford an approximate indication of the proportion of the admixture. If the adulterating oil can be identified by its chemical or physical characters, or referred to its proper group, the altered specific gravity of the sample will also afford a means of approximately estimating the proportion present. *Oleic acid* would not be detected by the alcohol test, but it can be determined with accuracy by titrating the sample with standard alkali.

The behavior of castor oil with petroleum spirit is highly characteristic. As far as has been recorded, all other fixed oils dissolve with facility in petroleum spirit, and are probably miscible in all proportions therewith, and with mineral lubricating oil. On the other hand, castor oil is not soluble in petroleum spirit, though it is itself capable of dissolving its own volume of that liquid. With the heavier petroleum and shale products castor oil behaves in a similar manner, at least in a qualitative sense. In making a mixed oil for lubricating purposes, the castor oil must first be dissolved in an equal measure of lard or tallow oil, and the heavy mineral oil subsequently added. If the proportion of this does not exceed that of the castor oil employed, no separation will occur on standing.

Castor oil is readily soluble in glacial acetic acid. It is easily miscible with an equal measure of that solvent at the ordinary temperature, whereas most other fixed oils, except croton oil, are only dissolved on heating, and yield solutions which become turbid before they have again cooled to the ordinary temperature.

Another useful test for the purity of castor oil is the determination of its saponification equivalent. The number for castor oil is about

315 The values found by the author for blown rape oil varied from 275 to 284. Most other oils require a larger proportion of alkali than castor oil, and this is especially the case with coconut oil, the presence of which the test is well adapted to recognise. Refined *rosin oil*, which has been extensively employed for the adulteration of castor oil, neutralises no alkali, or only a trifling quantity, and may be determined with accuracy by the process described on page 112. A sample of castor oil foots, containing much stearin, was found by the writer to have a saponification-equivalent of 295.3, the density being 939.4.

The formation of sebacic acid, when the sample is distilled alone or with a quantity of alkali insufficient for its complete saponification (p. 157), may be employed as a test for foreign fixed oils in castor oil.

#### ALIZARIN OIL. TURKEY-RED OIL.

In dyeing cotton goods red with alizarin, the employment of a fatty acid at one stage of the process is essential. Experience has shown that the best results are obtained by employing the ammonium salt of ricinolsulphuric acid,  $C_{18}H_{33}(HSO_3)O_2$ , a body which is obtained, mixed with unaltered esters and with the products of its decomposition (see "Sulpholeic Acid"), by the action of sulphuric acid on castor oil. The details of the method of preparation vary considerably; a common plan is to treat castor oil with strong sulphuric acid, added slowly with stirring, so that the temperature does not rise above 35° C. The excess of sulphuric acid is then removed by agitating the product with water and then with a solution of common salt, and the oily layer of crude ricinolsulphuric acid is neutralised with ammonia, or with a mixture of ammonia with potash or soda. The product consists chiefly of ammonium ricinolsulphate, and constitutes "alizarin or turkey-red oil," sometimes called "red oil" or "olein oil."

Turkey-red oil, if properly prepared from pure castor oil, when largely diluted, even with hard water,<sup>1</sup> will bear the addition of ammonium hydroxide to alkaline reaction without showing any turbidity on standing for several hours. A turbidity or precipitate denotes the presence of solid fats, and indicates the employment of either impure castor oil (*e.g.*, castor oil foots) or of rape, cottonseed, olive, or other oil containing stearin or palmitin. A further indication of these oils having been employed is obtained by boiling the sample for some time with dilute sulphuric acid, and observing the solidifying

<sup>1</sup> A pure turkey-red oil from castor oil can dissolve small proportions of calcium salts. If the oil be acid, a white precipitate may be produced on diluting it even with distilled water, but this will immediately disappear on adding excess of ammonium hydroxide.

point of the mixture of esters and free fatty acids constituting the oily layer. The alcohol test, described on page 158, is also available, for the oil layer will be wholly soluble if castor oil alone was used for the preparation of the alizarin oil, while the liquid will be turbid, and globules of undissolved matter will gradually separate, if other oils had been used. The test becomes more delicate if the alcohol be cautiously diluted.

The proportion of fatty acids, &c, present in alizarin oil varies considerably. It may be as low as 40, and occasionally reaches 65 per cent, the usual proportion being about 50 per cent.

For the determination of the total fatty matter Williams (*J S C. I.*, 1886, 73) treats 25 gm. of the sample in a porcelain dish on the water-bath with sufficient dilute acid to decompose it, 75 c.c. of a saturated solution of common salt, and 25 gm. of white wax. The ricinolsulphuric acid is insoluble in brine, and hence rises to the surface and dissolves in the melted wax. After cooling, the cake of wax is removed, dried as completely as possible with filter-paper, and then gently heated or dried over sulphuric acid to remove the last traces of water. The excess of weight over that of the wax taken gives the weight of fatty acids in the quantity of the original oil taken.

Bühl recommends the extraction of the liberated fatty acids with ether. The oil is treated with sufficient dilute sulphuric acid (1:10) for its decomposition, and is then shaken with ether. The ethereal layer is separated, evaporated at a gentle heat, the residue dried at a temperature not exceeding 70° C, and then weighed. Williams considers this process to give results in excess of the truth, in consequence of the ethereal extract being contaminated with water and mineral matter (usually sodium sulphate). The ethereal layer cannot be purified by agitation with water without some of the ricinolsulphuric acid passing into the aqueous liquid.

### Croton Oil.

*French*—Huile de croton    *German*—Crotonöl

(See also p. 95.) Croton oil is obtained from the seeds of the *Croton tiglium*.

The discrepancies in the analytic data for croton oil as determined by different observers are probably largely dependent upon the method by which the oil was obtained. Thus, Javillier (*Analyst*, 1898, 213) prepared three samples, the first by simple expression, the second by extraction with ether, and the third by digestion at 75° C, with 95

per cent. alcohol, the first two methods being those described by the French Codex of 1884. The yield and character of the products are shown in the following table —

	EXPRESSED OIL	OIL EXTRACTED BY ETHER	OIL EXTRACTED BY ALCOHOL
Yield . . .	12.5 per cent.	38 per cent.	12 per cent.
Color . . .	Pale	Light brown	Very dark brown
Solubility (1 vol of oil + 2 vols absolute alcohol)	Soluble at 75° C	Soluble at 75° C	Soluble in the cold
Solidification temperature . . .	—7° C	—7° C	—8° C
Iodine number . . .	109	108	91.2
Saponification value . . .	192.9	194.5	260.6
Acid value . . .	27.1	36.9	60.1

The acid value was determined by dissolving the oil in ether and titrating directly with decinormal alcoholic potash.

The lighter varieties darken very much with age. Croton oil differs from castor oil in being soluble in petroleum spirit. It has slight drying power and forms no elaidin with nitrous acid. It is stated to contain the following fatty acids and their esters —stearic, palmitic, oleic, myristic, lauric, valeric, butyric, acetic, formic, and tiglic. Dunstan and Boole (*J S C I*, 1895, 985) have shown that the vesicating constituent is a neutral, resinous substance of empirical formula  $C_{10}H_{16}O_4$ , which forms but a small proportion of the so-called "croton-oleic acid" from which it is obtained.

Lewkowitsch has observed Reichert-Meissl values of 13.27 and 13.56, and acetyl values of 19.61 and 20.02 for croton oil. The same observer gives a solidifying point of the mixed fatty acids as 18.6° to 19° C.

### Palm Oil.

*French*—Huile de palme *German*—Palmöl, Palmfett

(See also page 96.) Palm oil is the product of several species of palm, but particularly of *Elais Guineensis*. Palm oil proper is obtained from the outer fleshy coating of the seed, the palmitut or palm kernel oil having a different composition.

Palm oil varies in consistency from that of soft lard to that of the hardest tallow, and its melting point is correspondingly variable. In color the oil ranges from the brownish-yellow common in the Salt-pond and Grand Bassa brands through various shades of red and orange to the orange-yellow of Calabar oil. The color becomes pale after keeping, especially upon exposure to light and air, the oil at the

same time becoming rancid. The odor of some of the better qualities, such as Calabar, Brass, and Benin, is not disagreeable, but some of the irregular, such as Salt-pond, have a more or less disagreeable smell, especially when warmed.

In chemical composition fresh palm oil consists essentially of palmitin, olein, and palmitic acid.

Palm oil is a common constituent of railway-carriage grease, and is largely used for making soap. Palmitic acid, extensively employed for making candles, and oleic acid, often called "oleine," are obtained by saponifying palm oil under high pressure with water and a small proportion of a base, and subjecting the resultant mixture of fatty acids to hydraulic pressure.

Analytic data from the mixed fatty acids of palm oil have been given as follows —

Specific gravity at 98°-99° C (water at 15.5° = 1),	8369	(Allen)
Specific gravity at 100° C (water at 100° = 1),	8701	(Archbutt)
Solidifying point,	35.8°-46.2°, usually 44°-45°	
Melting point,	47.75°-50°	
Saponification value (mgrm KHO),	204-207	
Iodic value,	53.3	(Thoerner)

#### COMMERCIAL PALM OIL

Palm oil as met with in commerce varies greatly in quality. It almost always contains more or less water and solid impurities. Some of the irregular oils occasionally contain 25 or 30 per cent., but the usual range is from 2 to 16 per cent., while most of the regular oil does not contain more than 5 or 6 per cent. It is usual to sell palm oil on the assumption that 2 per cent. of such foreign matters are present; any excess over this is allowed for.

Water is best determined by exposing 10 grm of the sample to a temperature of 110° C for an hour or two, and noting the loss of weight (see "Lard"). If the residual oil be then dissolved in warm petroleum spirit, the *solid impurities* will settle to the bottom, and can be filtered off, washed with a little ether, dried, removed from the filter, and weighed. After weighing, the residue may be ignited, when the ash will indicate with sufficient accuracy the proportion of *sand* and *mineral matters*, and loss of weight will give that of the *organic matter*. In many cases the water can be determined with sufficient

accuracy by noting the measure of the aqueous layer which separates when the undried sample is dissolved in petroleum spirit, or simply kept melted in a graduated tube immersed in hot water.

Palm oil often contains a considerable proportion of *free fatty acids*, the amount increasing as the oil gets old. The free acid raises the solidifying point of the oil, and causes it to exercise a very corrosive action on iron and steel. A strip of bright steel will soon become discolored if immersed in palm oil containing free acid, and if left for some time in the oil will be found to be deeply pitted in places. The following proportions, calculated as palmitic acid (see page 105), have been found —

KIND OF OIL	PALMITIC ACID, PER CENT		KIND OF OIL	PALMITIC ACID, PER CENT
	Archbutt	A. N. Tate		I. Archbutt
Salt-pond . . .	78.9	84.6	Fernando Po .	10.5
Unknown . . .	72.6	..	Hull-jack . . .	35.7
Refined . . .	55.8	..	Hull-jack . . .	24.4
Brass . . .	53.2	60.0	Bonny . . .	21.3
New Calabar .	52.2	100.0	Lagos . . .	11.9

The following results obtained by the analysis of typical samples of palm oil, from which the water and impurities were removed, have been communicated to the author by A. Norman Tate —

	BRASS	BENIN	LACON	NEW CALABAR	OLD CALABAR	GRAND RIVER
Specific gravity at 15° C.	914	922.8	910.3	9269	9209	9215
Saponification-equivalent	289.2	284.9	285.1	289.9	281.5	278.8
Fatty acids, percent age	96-97	96-96.5	94-97	94-97	91.2-95	95.5-96.5
" solidifying point	44.1-45.8	45.0-45.5	44.7-45.5	11.2-15.6	11.2-15.5	11.5-12.3
" combining weight,	273.1	273.7	272.7	271.2	271.2	270.0

**PALM OLEIN** is obtained by subjecting palm oil to hydraulic pressure in the same way that lard oil is made from lard. It usually has a density of about 914, and solidifies at 10° C. With sulphuric acid it gives a greenish-yellow spot, which changes to a mottled brown on stirring.

**PALM NUT OIL** or **PALM-KERNEL OIL** presents marked distinctions from palm oil. It varies from white to primrose yellow or pink in color, with a characteristic odor recalling that of violets, but not unlike that of coconut oil, which it resembles closely in every respect. The density is high, ranging from 866 to 873 at 99° C. (compared with water at 15.5°). The melting point is from 26° to 30°, solidification

occurring at 18° to 20°, and the temperature again rising pretty constantly to 25° or 26° C.

Palmnut oil contains a large proportion of esters of lower fatty acids, the composition of a sample analysed by Oudemans being—

Olein, . . . . .	26.6 per cent
Stearin, palmitin, and myristin, . . . .	33.0 „
Laurin, caprin, caprylin, and caprom, . . .	40.4 „
	<hr/>
	100.0 „

It is worthy of notice that all the fatty acids of which the esters are said to be present contain an even number of carbon atoms. The same remark applies to coconut oil, which has a very similar composition (see page 166), but usually contains a somewhat larger proportion of lower fatty acids. Thus, the saponification-equivalent of palmnut oil usually is about 227, but varies somewhat with the mode of preparation. If it be extracted from the palm-kernels by a solvent instead of by pressure the proportion of higher fatty acids is increased, and the melting point and saponification-equivalent of the product are raised in proportion. Palmnut oil is stated to be sometimes adulterated with or substituted by lard or tallow, colored with turmeric and scented with orris root. With modified figures for the saponification-equivalent and distillate acidity (page 58), the method of examining coconut oil for such adulterants fully applies to palmnut oil.

The following are some analytic data from the mixed fatty acids of palmnut oil:—

Solidifying point (titer test),	20°–25.5° C.	(Lewkowitsch)
Melting point,	20.7°–28.5°.	
Iodine value,	12.0	
Refractive index,	1.431	(Thoerner)

#### Cacao Butter. Oil of Theobroma.

*French*—Beurre de cacao. *German*—Kakaobutter.

(See also page 96.) This oil is expressed from the cacao-nut, *Theobroma cacao*, from which ordinary cocoa is obtained, and must not be confused with coconut oil from *Cocos nucifera*.

Cacao butter is a yellowish solid, gradually turning white on keeping. At the ordinary temperature it may be broken into fragments, but softens in the hand and melts in the mouth. It fuses between 30° and 34° (rarely at 29°) to a transparent yellowish liquid, which congeals again at 20.5°, the temperature rising to about 27°. It has an



agreeable odor, tastes like chocolate, and does not readily become rancid. It dissolves in 20 parts of hot alcohol, separating almost completely on cooling, and is also dissolved by ether and acetic ether.

Cacao butter contains stearin, olein, and a little laurin, palmitin, and arachidin. C. Kingzett obtained from cacao butter an acid of the formula  $C_{64}H_{128}O_2$ , which he named theobromic acid.

#### EXAMINATION OF CACAO BUTTER

Cacao butter is liable to adulteration with tallow, lard, stearic acid, paraffin wax, coconut, almond, arachis and other oils. Observations of the melting point and specific gravity do not furnish satisfactory means of detecting such admixtures. Determinations of the iodine number, acid number, and saponification-equivalent are the most satisfactory in detecting adulteration. The iodine number usually ranges between 33 and 37.5. Strohl has found the high figure 41.7 per cent. The saponification-equivalent ranges from 278 to 292, and is usually about 287. That of coconut oil is about 250. Stearic acid is indicated by the increased acid value and paraffin wax or beeswax by the increased saponification-equivalent. R. Benzenemann finds the fatty acids from different kinds of cacao butter to have a very constant melting point. When the determination is made in the manner recommended by him (page 35), they commence to melt at  $48^{\circ}$  to  $50^{\circ}$ , the temperature of perfect fusion being  $51^{\circ}$  to  $53^{\circ}$  C. Tallow is said to be capable of detection by saturating a cotton thread with the oil, allowing it to burn for a short time, and then blowing it out, when the odor of tallow becomes perceptible.

A better test for tallow and other adulterants of cacao butter is to dissolve 2 grm. of the fat in 4 grm. of ether at  $17^{\circ}$  C, and then immerse the closely corked test-tube in ice-cold water. Granules will separate from pure cacao butter in not less than 3, and more frequently in from 5 to 8 minutes, while if tallow be present a turbidity will appear at once or within  $2\frac{1}{2}$  minutes, according to the proportion of the adulterant, of which 5 per cent may thus be detected. On exposing the solution to a temperature of  $14^{\circ}$  to  $15^{\circ}$ , it will gradually become clear again if the sample was pure, but not if it was adulterated. This test is due to Bjorkland, and is adopted in the United States Pharmacopoeia. Its value has been confirmed by other observers, of whom Lamhofer has pointed out that petroleum ether may be employed with similar results, except that the cacao butter separates rather more slowly than from ether, the deposit being always granular, while other fats render the entire liquid cloudy. The solution of cacao butter in

two parts of ether will remain clear for a whole day if maintained at a temperature of 12° to 15°. This modification of the test is prescribed by the German Pharmacopœia, and is due to Ramsperger, who states that aniline may be substituted for the ether.

According to E. Dietrich, a very reliable test for the purity of cacao butter consists in warming the sample with an equal quantity of "paraffin oil." A drop of the mixture is placed on a slip of glass, a thin cover applied and slightly pressed down, and the slide then exposed for twelve hours to a temperature not exceeding 5° C. When then examined with polarised light under a magnifying power of 20 diameters, cacao butter appears crystallised in a form resembling palm-leaves, showing a fine play of colors with selenite. An addition of 10 per cent of beef tallow causes the fat to crystallise in tufts of needles, which exhibit a black cross, while, if mutton tallow be the adulterant, it is stated that no cross can be seen.

The following are analytic data from the mixed fatty acids of cacao butter —

Solidifying point (titer test),	48°-48.27°	(Lewkowitsch)
Melting point,	48-53°	
Saponification value		
(mgrm KHO),	190	(Thoerner)
Iodine value,	32.6-39.1	
Refractive index,	1.422	(Thoerner)

### Coconut Oil.

*French*—Beurre de coco    *German*—Kocosnussol.

(See also page 97.) Coconut oil has the consistency of butter or soft lard. It is white or but slightly colored, and has a characteristic taste and odor of coconut. It is liable to become rancid, and has then a less pleasant flavor. The melting point is variable, and the specific gravity at 98° to 99° C ranges from .866 to .874, being greater than that of the majority of vegetable fats.

Coconut oil has a peculiar and highly complex chemical composition. It is largely composed of laurin, and contains even lower homologues (*e g*, caprin, caprylin, caproin), which yield acids capable of distillation in a current of open steam, and to some extent soluble in water (see pages 51 and 59); but myristin, palmitin, and stearin are also present in notable proportion. On the other hand, the low iodine-absorption (8.0 to 9.5) shows that comparatively little olein or its homologues can be present. C. R. A. Wright states that the mixed fatty acids from coconut oil have a mean combining weight ranging between 196 and 204, that of

pure lauric acid being 200. The saponification-equivalent of coconut oil varies from 209 to 228, the corresponding mean combining weights (calculated) of the mixed fatty acids ranging from 195.7 to 214.7. Coconut oil forms a soap the aqueous solution of which is not readily precipitated by common salt, and hence is available for use with sea-water.

The following figures have been obtained from the mixed fatty acid of coconut oil —

Specific gravity at 98°-99° C (water at 15.5° = 1),	8354	(Allan)
Solidifying point (titer test),	21.2°-25.2°	(Lewkowitsch)
Melting point,	24°-27°	
Saponification value (mgrm of KHO),	258	(Thoerner)
Iodine value,	84-85	
Refractive index,	1.4395	(Thoerner)

Coconut oil is alleged to be liable to adulteration with suet, beef marrow, and other animal greases, as also with almond oil and wax. These would be detected by the reduced specific gravity at the temperature of boiling water, the increased saponification equivalent, and the reduced amount of alkali neutralised by the distillate obtained by Reichert's process. Indeed, there is no addition likely to be made in practice, excepting that of palmnut oil, which, if practised in notable proportion, would not be detected by these tests. The same methods if used with discretion will equally serve to determine the approximate proportion of the adulterant. *Palmnut oil* cannot be detected by the above or any other satisfactory method, but as it is employed for the same purposes as coconut oil, the substitution has little practical importance.

COCONUT OLEIN and COCONUT STEARIN are products obtained by submitting coconut oil to hydraulic pressure. The following figures, obtained in the author's laboratory from samples furnished him by Price's Patent Candle Company, show the relative physical and chemical characters of the two products —

	OLEIN	STEARIN
Sp. gravity (water at 15.5°) —		
At 98.5° C,	8710	8606
At 60.0° C,		8959
At 15.5° C,	9262	Solid
Melting point, °C,		28.5
Solidifying point, °C,	4.0, rising to 8.0	21.5, rising to 26.0
Saponification equivalent,	215	217
No. of c $\frac{N}{10}$ alkali by Reichert's test,	5.6	3.1

By treatment with alcohol and animal charcoal a neutral coconut oil is produced, which is sold under the names "vegetable butter," "vegetaline," "lactine," "nucoline," "laureol," &c. When well prepared these are white, of about the consistency of butter, of agreeable, sweet flavor, and, according to Jean (*J S C I*, 1891, 275), free from tendency to become rancid.

Coconut oil is frequently used in the preparation of margarine.

### Japan Wax.

*French*—Cire de japon    *German*—Japanisches Wachs

(See also page 97) Japan "wax" is a fat contained between the kernel and outer skin of the berries of several species of *Rhus*, the most important of which is *Rhus succedanea*, which flourishes chiefly in the western provinces of Japan, and is now also cultivated in California. The crude wax forms a coarse, greenish, tallow-like mass, which is purified by melting, pressing through canvas, and bleaching in the sun.

The purified wax is a yellowish-white, straw-yellow, or greenish-yellow, wax-like mass, having a smell recalling at once that of tallow and of some kinds of beeswax. Under ordinary circumstances it fuses at  $51^{\circ}$  to  $53^{\circ}$  C., but a recently solidified sample melts at a considerably lower temperature. Its solidifying point is about  $41^{\circ}$ , the temperature rising to  $48$ – $49^{\circ}$  in the act of solidification. The specific gravity at the ordinary temperature is about 990, while in a molten state at a temperature of  $98^{\circ}$  to  $99^{\circ}$  C it is 873 to 877, compared with water at  $15.5^{\circ}$  C. Thus, in the solid state it agrees in specific gravity with the true waxes, and in the molten state it is considerably heavier than the true waxes or the ordinary vegetable fats. It is completely soluble in boiling alcohol, but is almost completely deposited on cooling.

Japan wax is stated to be frequently adulterated with water, with which it is capable of forming a sort of emulsion when agitated with it a little above its melting point.

It is readily and completely saponifiable, yielding glycerol, and hence is distinct in constitution from the true waxes, which yield monatomic alcohols when saponified (page 45). It consists essentially of palmitin, laurin, and small amounts of stearin and arachidin, with more or less free palmitic and lauric acids. The following figures were obtained in the author's laboratory by the examination of three samples from different sources. For convenience, the results yielded by a sample of myrtle wax are placed in juxtaposition —

	JAPAN WAX			MYRTLE WAX
	No 1	No 2	No 3	
Specific gravity of solid wax at 15.5° C . . .	..	903	994	
Specific gravity of molten wax at 98-99° C . .	876	877	876	875
Melting point (method a, page 34) . . . .		51.5	52.0	40.5
Solidifying point (method d, page 37) . . . .		..	41.0	39.5
" " temperature rising to . . . .			48.5	39.5
Free fatty acid, per cent (in terms of palmitic acid) . . . .	9.03	12.72	8.06	9.12
Saponification-equivalent . . . .	258.7	252.9	261.2	265.2
" Percentage of KHO required . . . .	21.68	22.14	21.11	21.15
Products of saponification —				
Glycerol, per cent . . . .	13.50	14.71	11.90	13.38
Insoluble acids, sp. gr. at 98-99° C . . . .		918	818	827
" melting point . . . .	57.0	..	56.0	47.5
" solidifying point . . . .	..	56.5	54.0	46.0
" combining weight . . . .	..	259.3	257.5	244.0
Soluble acids ( $C_{14}H_{25}O_2$ ) per cent . . . .	..	..	8.10	..

The specific gravity of the insoluble acids, considered in conjunction with their mean combining weight, renders it doubtful whether these fatty acids really consist of palmitic acid with more or less of its homologues, or of fatty acids isomeric with these.

The mixed fatty acids of Japan wax have given the following data.—

Specific gravity at 98° to 99° C		
(water at 15.5° = 1),	818	(Allen)
Solidifying point,	53°-59.4°	
Melting point,	56°-57°	(Allen)

The proportion of glycerol, as determined by the permanganate process, produced by the saponification of Japan wax is notably in excess of that required to form a triglyceride of the fatty acids present, and this is especially true of No. 2, the glycerol from which sample was several times determined with great care. Whether the high proportion of glycerol be real, or due to some unusual constituent which renders the determination by permanganate inaccurate, has not been positively ascertained.

That the constitution of Japan wax is peculiar is evident from the study of the products of its saponification, and is shown also by its high density both in the solid and liquid state, in which characters it differs widely from the majority of solid fats. La Wall (*J S C. I.*, 1897, 247), notes the adulteration of Japan wax with starch to the extent of 25 per cent. Adulteration with water is also practised. The addition of tallow may be detected by the lowered melting point and

increased iodine absorption. The iodine absorption of pure Japan wax ranges between 4.2 and 6.6 per cent.

### Tallow

*French*—Suif *German*—Talg.

(See also page 99.) Tallow is commercially classed as "beef" and "mutton" tallow, but each of these comprises the fat of other animals besides the ox and sheep.

Pure tallow is white and almost tasteless, but much of that in commerce has a yellow color and disagreeable rancid flavor.

In chemical composition, tallow is very similar to lard, consisting essentially of a mixture of palmitin, stearin, and olein. According to A. Schuller, tallow can be distilled in a vacuum, if distilled with superheated steam it yields oleic, palmitic, and stearic acids, and glycerol. The relative proportions of oleic and solid fatty acids yielded on saponification affect the value of tallow (see below).

By pressure, a considerable portion of the olein of tallow can be removed, and forms a product known as "tallow oil" (page 173), the solid portion constituting "tallow stearin."

The following are analytic data from the mixed fatty acids of tallow —

#### BEEF TALLOW

Specific gravity at 100° C (water at 100° = 1),	8698	(Archbutt.)
Solidifying point (titer test),	38°-46°, usually 43°-45°	
Melting point,	43°-47°	
Saponification value (mgrm. KHO),	197.2-201.6	
Iodine value,	20-41	
Iodine value of liquid fatty acids,	92.2-92.4	(Wallenstein and Finck.)
Refractive index	1.4375	(Thoerner.)
Oleo-refractometer,	-40	(Jean.)

#### MUTTON TALLOW

Solidifying point (titer test),	40°-48°, usually 43°-46°	
Melting point,	46°-54°	
Saponification value (mgrm. KHO),	210	(Thoerner.)
Iodine value,	34.8	(Thoerner.)
Iodine value of liquid acids,	92.7	(Wallenstein and Finck.)
Refractive index,	1.4374	(Thoerner.)

## EXAMINATION OF COMMERCIAL TALLOW

The tallow of commerce frequently contains a sensible proportion of *free fatty acid*, the amount of which can be ascertained with accuracy by titration with standard alkali and phenolphthalein, as described on page 105. The percentage of potassium hydroxide (KHO) required for neutralisation, when multiplied by 5, gives with sufficient accuracy the percentage of free acid. W. H. Deering (*J S C I*, 1884, 540) found that in 24 out of 25 samples of tallow from different sources the free acid ranged from 0.85 (in an Australian mutton tallow) to 12.20 per cent. (in a Russian tallow), while one sample ("town tallow") which had been kept in store for six years contained 25 per cent. of free fatty acids. The free acid in 36 samples of Australian tallow examined by A. N. Tate ranged from 1.20 to 4.70 per cent. Large proportions of free acid are apt to be due to the tallow being adulterated with wool-grease acids, or stearic acid from cottonseed oil.

Tallow frequently contains more or less water, infusible matters, and mineral impurities, and has been occasionally purposely adulterated with starch, china clay, whiting, barium sulphate, &c. Fats of greater fusibility, especially bone fat, may be present, and wool grease acids and cottonseed "stearin" have been extensively used. Cakes of tallow are said to have been met with the interior of which consisted of inferior fats.

The presence of *water*, *starch*, and *insoluble substances* generally can be detected, and their proportion estimated, as described under "Lard". The insoluble matter present in samples of tallow representing large lots is usually under 0.2 per cent., and the water rarely exceeds 1 to 1.5 per cent. If *bone fat* be present, the calcium phosphate, which is a characteristic constituent of it, is not separated by simple fusion, but will be left with any other mineral impurities on igniting the tallow in a muffle. For the detection of calcium phosphate and other impurities, 10 grm. of the tallow may be dissolved in carbon disulphide or petroleum spirit, filtered, the residue washed with a little ether, and dried at a moderate temperature. The insoluble matter may be examined under the microscope, when *starch*, *gelatinous matter*, or fragments of *tissue* will be readily recognised. Starch may also be detected by boiling the residue with water and testing the solution with iodine. *Lime soap* will be detected by warming the residue with dilute hydrochloric acid, when globules of fatty acids will rise to the top of the liquid, and the latter, after filtration, may be neutralised and tested for calcium

with ammonium oxalate. Any effervescence of the residue, on addition of hydrochloric acid, will probably be due to *whiting*. Resin and resin oils, paraffin wax, coconut oil, cottonseed oil, and cottonseed stearin are more or less common adulterants of tallow. The quantitative reactions in conjunction with the special tests will usually suffice for their detection. (Compare "Lard.")

Tallow which has not been washed and purified, and which therefore contains particles of blood, &c., acquires a light brown color when agitated in a melted state with one-fifth of its measure of nitric acid (sp. gr. 1.38). This reaction was formerly erroneously ascribed to the presence of cottonseed stearin.

The varying quality and frequent adulteration of tallow some years since caused the French candle-manufacturers to adopt a process of assaying samples for the relative proportions of oleic and solid fatty acids. This they effect by Dalcian's method, which consists in determining the solidifying point of the mixed fatty acids produced by saponifying the fat by method *d*, page 37 (titer test). The lowest permissible solidifying point of the acids is often fixed at 44° C., corresponding to a mixture of oleic and solid fatty acids in equal proportions. The following table by F. Dalcian shows the approximate yield of *solid fatty acids* ("stearic acid") from 100 parts of tallow or other fat. The corresponding *oleic acid* may be found by subtracting the percentage of solid acids from 95.00.

SOLIDIFYING POINT, °C	SOLID ACIDS, PER CENT	SOLIDIFYING POINT, °C	SOLID ACIDS, PER CENT	SOLIDIFYING POINT, °C	SOLID ACIDS, PER CENT
40.0	35.15	43.5	44.65	47.0	57.95
40.5	36.10	44.0	47.50	47.5	58.90
41.0	38.00	44.5	49.40	48.0	61.75
41.5	38.95	45.0	51.30	48.5	66.60
42.0	39.90	45.5	52.25	49.0	71.25
42.5	42.75	46.0	53.20	49.5	72.20
43.0	43.70	46.5	55.10	50.0	75.05

Tallow has been occasionally met with which has been largely adulterated with the distilled *fatty acids from wool grease*, and L. Meyer (*Dingl. polyt. J.*, cxxlviii 305) has described a sample which consisted almost exclusively of such fatty acids. It smelt strongly of wool grease, yielded only 0.2 per cent of glycerol on saponification, and when the aqueous solution of the soap was shaken with ether, and the ethereal solution separated and evaporated, a considerable amount of cholesterol was obtained, which gave a violet coloration



changing to blue when evaporated with concentrated hydrochloric acid and ferric chloride. Meyer states that 5 per cent of wool grease can be detected in tallow by this method. The fatty acids separated from the soap formed in the above process turned yellow in a few days, and after several months had acquired a deep orange-yellow tint.

TALLOW OIL, or Tallow Olein, is obtained by submitting tallow to hydraulic pressure. It much resembles lard oil, but is usually of inferior quality. The name "tallow oil" is sometimes incorrectly applied to crude oleic acid.

### Lard.

*French*—Saindoux. *German*—Schmalz.

(See also page 99.) Lard is the fat of the pig, melted and strained to separate tissue and impurities. The kind known as "bladder lard" or leaf lard is usually prepared solely from the *omentum* or fat surrounding the kidneys. "Keg-lard" is made from the fat of the entire animal, and usually melts between 28° and 38° C, and solidifies between 24° and 31°; hence it melts at a lower temperature than that from the *omentum*, which fuses at 42° to 45° C, and alone has the right to be called lard. The mixed fat from the entire animal would be more appropriately termed "hog-dripping," and evidently bears the same relation to lard proper that mutton or beef dripping bears to suet.

The *Adeps preparatus* of the *British Pharmacopœia* is directed to be prepared from "the internal fat of the abdomen of the hog, perfectly fresh"; and is stated to melt at about 37.5° C.

By subjecting lard to a moderate temperature, combined with hydraulic pressure, most of the olein is separated, and forms lard oil, while the stearin and palmitin remain in the form of a solid cake of high melting point.

The following are analytical data from the mixed fatty acids of lard —

Specific gravity at 98°–100° C (water at 15.5° = 1),	837–840	(Allen)
Solidifying point,	34°–41°	
Melting point,	35°–47°.	
Iodine value,	58–65	
Iodine value of liquid fatty acids,	90°–100°.	
Refractive index,	1.4395	(Thoerner.)
Oleo refractometer,	–30°.	(Jean.)

## EXAMINATION OF COMMERCIAL LARD

*Sodium carbonate* is sometimes added to the melted lard, with a view of whitening the product. Milk of *lime*, used in the proportion of from 2 to 5 per cent, gives a pearly white product, with which a large amount of water can be incorporated by stirring during cooling. *Potato starch* and *alum* have been occasionally mixed with lard. Pure lard is wholly free from taste or smell, and forms a perfectly clear liquid when melted by immersing the tube containing it in hot water. If either lime, sodium carbonate, water, or any similar addition has been made, the melted fat will be more or less opaque. Adulteration by water seems to be less common than formerly. Its amount may be estimated by heating 10 grm of the sample at a temperature of 110° C until no more globules of water can be seen and determining the loss in weight.

*Coconut oil* has been employed for adulterating lard; arachis and sesame oils are said to be used. The adulteration of lard most frequently practised consists in the addition of cottonseed oil, cottonseed, and beef stearin. Mixtures of beef stearin and cottonseed oil, containing no lard, are often sold under the name "lard compound" or "compound lard." The presence of cottonseed stearin or coconut oil would be indicated by the increased specific gravity, as will be seen by the following figures —

	LARD	COCONUT OIL	COTTONSEED STEARIN
Specific gravity at 98° to 99° C (water at 15.5° C = 1)	860 to 861	868 to 874	
Specific gravity at 100° F (water at 100° F = 1)	905 to 907	910 to 916	911 to 912
Melting point, °C . . . . .	33 to 45	20 to 28	32
Saponification-equivalent . . . . .	286 to 292	200 to 228	285 to 294
Iodine-absorption	59 to 62	9	.

Coconut oil will also be detected by the Reichert test.

Arachis oil may be detected by Renard's test (see "Arachis Oil"), and sesame oil by the furfural reaction. Cottonseed oil may be detected by Becchi's test, but instances have been reported in which pure lard (or the fatty acids from it) from pigs fed on cottonseed meal responded to this test. Lard that has been exposed to air will also have a slight reducing effect on silver nitrate, and care should be taken, therefore, to select a sample from the interior of the mass. Halphen's test is less responsive to these conditions and will be found more generally satis-

factory than Becchi's test. The color-reaction with nitric acid is also a valuable indication of the presence of cottonseed oil, but it must not be forgotten that some samples of pure lard give a brown coloration with this reagent. Previous heating of the oil to  $240^{\circ}$  C. has no effect on the reaction.

Determination of the iodine absorption of the liquid fatty acids appears to be the most reliable method of detecting the addition of vegetable oils and fats to lard. In the case of European lards, the iodine value of the liquid fatty acids varies from 90 to 96, and in American lards it may range from 97 to 106. If, therefore, the iodine value of the liquid acids of a sample be found to be above these limits, adulteration with a vegetable oil is proved; if coconut or palm-kernel oil be present, the figure will be lower. See under head of "Liquid Fatty Acids" for the method of their separation and data relating to them.

Von Raumer (*Analyst*, 1897, 265) calls attention to the possible value of Schiff's reagent (see vol. I, p. 219) as a means of distinguishing between rancid and overheated lards and those adulterated with cottonseed oil, all of which respond to Becchi's test. Five c.c. of the melted fat were shaken with 10 c.c. of the reagent and placed in water at  $90^{\circ}$  C. for two or three minutes. Fresh lard either gave no color at all or at most a faint rose, which disappeared in about thirty minutes when cold; slightly rancid lards gave a strong color, which disappeared more slowly, but strongly rancid and overheated lards gave a pronounced violet, which did not disappear on cooling. On the other hand, beef stearin and beef stearin containing 30 to 40 per cent of cottonseed oil showed no coloration.

Jones (*Analyst*, 1888, 170) detects the presence of cottonseed oil by the use of sulphur chloride, as follows. The fat is melted and 5 gm. run by means of a pipette into a porcelain dish. Just before solidification 2 c.c. of a mixture of equal parts of sulphur chloride and carbon disulphide are added. At the time of this addition the mass should be well stirred and also occasionally during the succeeding fifteen minutes. Under this treatment genuine lard only thickens or may become rather stiff in three hours, but if any considerable proportion of cottonseed oil be present the mass becomes quite hard in half this time. Lewkowitsch has found this method useful.

Cottonseed stearin remains fluid for some time at a comparatively low temperature after being once melted, so that a sample containing it, when allowed to cool after fusion, does not set so solid as at first.

The rise of temperature with sulphuric acid, or, better, with bromine, will often furnish useful results in the detection of cottonseed oil. Examination in the oleo-refractometer may also be of value.

For the detection of beef stearin in lard, Stock's modification of Belfield's test is the most satisfactory; it consists in comparing the crystals obtained from an ethereal solution with those from two standard sets of mixtures, the first consisting of pure lard melting at  $34^{\circ}\text{C}$ . to  $35^{\circ}\text{C}$ ., with 5, 10, 15, and 20 per cent. of beef stearin melting at  $56^{\circ}$ , the second of pure lard, of melting point of  $39^{\circ}$  to  $40^{\circ}$ , with 5, 10, 15, and 20 per cent. of beef stearin melting at  $50^{\circ}$ . The process is as follows. The melting point of the sample is determined by the capillary tube method. Suppose the melting point be found at  $34^{\circ}$ , 3 c.c. of the melted fat are run into a graduated cylinder of about 25 c.c. capacity; 21 c.c. of ether are added, and the fat dissolved at  $20^{\circ}$  to  $25^{\circ}$ , 3 c.c. of each of the first set of mixtures are treated in exactly the same way. The five cylinders are cooled down to  $13^{\circ}$ , and allowed to remain at that temperature for twenty-four hours. An approximate estimate as to the amount of the adulterant is arrived at by reading off the apparent volume of the deposited crystals. The ether is then poured off as far as possible, and 10 c.c. of fresh ether at  $13^{\circ}$  is added in each case. The cylinders are again shaken, cooled as before, and the proportion of crystals read off as before. Finally, the contents of the cylinders are emptied into weighed shallow beakers, the ether drained off carefully, the mass allowed to dry for fifteen minutes at  $100^{\circ}$  and weighed. The weight obtained for the sample under examination is compared with the weight of the crystals obtained from whichever of the standards comes nearest to it. The second set of mixtures is used for samples of higher melting point. The actual presence of beef fat must be proved by microscopical examination, when the characteristic tufts are seen. No sample of pure lard melting below  $39^{\circ}$  yielded more than 0.011 grm. of crystals under the above conditions. A sample of the melting point  $45.8^{\circ}$  gave, however, 0.146 grm. of crystals.

Cochran (*J. A. C. S.*, 1897, 796) finds the following method more delicate than the direct solution in ether. Two c.c. of the melted fat are mixed with 22 c.c. of fusel oil and the mixture warmed to about blood heat, and when complete solution is effected it is allowed to cool slowly to  $16^{\circ}$  or  $17^{\circ}\text{C}$  and maintained at this temperature for several hours, during which a crystalline deposit forms. This is transferred to a filter, the fusel oil drained off as far as possible, and a part or whole of the residue dissolved in ether in a test-tube, the mouth of the

tube plugged with cotton. The crystals which form on standing may be mounted in cottonseed oil and examined under the microscope.

*Mineral additions* will be left on igniting the lard, a little at a time, in a porcelain dish. *Salt, alum*, and other soluble mineral additions can also be dissolved out by agitating the melted lard with hot water, and identified by testing the aqueous liquid with suitable reagents. *Lime* may be detected by triturating the sample with calomel or a solution of mercurous nitrate, when more or less darkening will ensue if lime be present. *Lime soap* may be detected as in tallow.

The presence of *gelatinous matter* has been observed in lard by several chemists. It is probably usually a product of the alkali employed in refining on the albuminous matters present; but appears in some cases to have been derived from Irish moss.

#### LARD OIL

When lard, especially the softer kind, is subjected to hydraulic pressure, it yields a considerable quantity of a fluid called "lard oil," or "lard olein," while the solid portion constitutes "pressed lard," or "lard stearin." Consequently, the melting point and other characters of lard oil depend much on the temperature at which the pressing is conducted, winter-pressed lard oil naturally containing less of the solid constituents of lard than that expressed at a higher temperature.

Lard oil consists of olein, with variable proportions of palmitin and stearin. It varies in tint from light yellow to colorless, and has but little odor. It usually thickens at about  $4^{\circ}\text{C}$ , and becomes solid at  $-4^{\circ}\text{C}$ , but some samples exhibit wide departures from these limits. A specimen of pure winter-pressed oil examined by J. Henry began to deposit flakes at  $-8^{\circ}$ , was thick at  $-10^{\circ}$ , and solid at  $-12^{\circ}\text{C}$ . It did not remelt completely until the temperature reached  $+7^{\circ}\text{C}$ .

In many of its reactions, as in its chemical composition, lard oil closely resembles olive oil, which it simulates in its behavior with nitric acid, the elaidin-test, and the temperature produced by strong sulphuric acid.

Lard oil is extensively employed as a lubricant. The chief adulterants affect its viscosity and non-drying characters, and therefore its value for lubricating. Lard oil should not show any notable proportion of *free acid* when examined as on page 105. Lard oil is often employed in lighthouse and signal lamps, and a small percentage of free acid or of cottonseed oil affects, injuriously, its quality for these purposes.

The specific gravity of lard oil is about 915, and should not exceed 916 at 15.5° C. If greater, the specimen is probably adulterated with fish oil, coconut olein, or cotton or other seed oil. *Fish oils* can be detected by the odor on warming the sample, by the increased temperature with sulphuric acid, and by the color-reactions with sulphuric acid and caustic alkali; *coconut olein* may be recognised by the taste and modified saponification-equivalent of the sample, and cotton and other *seed oils* may be detected, as in olive oil, by the elaidin-test, and their color-reactions with nitric acid.

*Rape oil* has nearly the same specific gravity and color as some samples of lard oil. It may be detected by the modified elaidin reaction and color-reaction with nitric acid, by the increased temperature developed on treating the sample with sulphuric acid; by the increased saponification-equivalent, and by the behavior of the sample when heated to about 200° C, and then allowed to cool to 30°. Lard oil is deodorised by this treatment, whereas the peculiar penetrating smell of rape oil is enhanced.

Lard oil has also been adulterated with a highly refined *earthnut oil*, manufactured in France. The admixture will be indicated by the behavior of the sample with nitric acid (page 86), and by the process described on page 134, depending on the isolation of arachidic acid.

The presence of many vegetable oils in lard oils is indicated by the appearance of a well-defined band in the absorption-spectrum, near the line B. Genuine lard oil gives no absorption-bands.

*Hydrocarbons* can be detected and determined as described on page 112.

### Butter-fat.

*French*—Gras de beurre. *German*—Butterfett.

(See also page 99.) Butter-fat is the fat of milk or butter. When used without qualification the term "butter-fat" is always to be understood as applying to the fat from cows' milk, but the milk of other animals yields a similar product.

Butter-fat can be prepared direct from milk by rendering the liquid faintly alkaline with caustic soda, and then agitating it with ether. After standing at rest for some time the ether separates, and can be removed and distilled, when the butter-fat remains. It may also be prepared by evaporating the milk to dryness at 100°, and exhausting the residue with ether or petroleum spirit. Butter-fat is, however,

more conveniently prepared from butter in the manner described on page 185.

Butter-fat has the well-known color, taste, and smell of butter. The melting and solidifying points vary considerably in different samples. According to J. Bell, the melting point usually ranges between  $29.5^{\circ}$  and  $33.0^{\circ}$  C, the maximum being  $34.7^{\circ}$ <sup>1</sup>. The specific gravity is higher than that of the majority of fats, a fact which is of some value for its identification.

Butter-fat has a peculiar and complex composition. The characteristic constituent is the radicle of butyric acid, which is present together with those of certain of its higher homologues.

James Bell obtained the following products by saponifying 100 parts of butter-fat. The fatty acids soluble in water were regarded as butyric acid. Those soluble in hot water only appear in the analysis as caproic acid, &c, the combining weight being deduced from the amount of barium carbonate left on igniting their barium salts:—

Butyric acid, . . . . .	6.13	.
Caproic, caprylic, and capric acids, . . . . .	2.09	(mean combining weight = 136)
Myristic, palmitic, and stearic acids, . . . . .	49.16	} = 85.56
Oleic acid, . . . . .	36.10	
Glycerol (calculated), . . . . .	12.54	
	<hr/> 106.32	

The proportion of butyric acid and its immediate homologues produced by the saponification of butter ranges between 5 and 8 per cent. Mutter obtained, from two samples of butter-fat, 40.4 and 34.8 per cent. of oleic acid, and 47.5 and 52.1 per cent. of mixed myristic, palmitic, and stearic acids.

The proportion of glycerol produced by the saponification of butter was first determined in 1823 by Chevreul, who obtained 11.85 per cent. by direct weighing of the isolated glycerol, and Liebschutz has isolated 13.75 per cent. By oxidising the glycerol with permanganate, and determining the oxalic acid formed, Benedikt and Zsigmondy have found from 10.2 to 11.6 per cent. of glycerol to be formed by the saponification of butter, and the author's figures fully confirm these.

These analytical results show that butter-fat is essentially a mixture of various esters, those of butyric, palmitic, and oleic acids being the

<sup>1</sup> Bell's melting points were determined by suddenly cooling the melted fat by immersing the platinum capsule containing it in ice-water. A fragment of the fat was then taken up on a loop of platinum wire, and gradually heated in water in close proximity to the bulb of an immersed thermometer.

leading constituents. Hehner and Mitchell obtained but very small proportions of stearic acid, and in some cases none.

Some experiments of James Bell indicate that several acid-radicles are present in the same molecule, and that butyrim cannot be separated by any process of fractional solution from the less soluble esters. Hence butter-fat probably contains complex esters of the following type —



Such a compound would yield fatty acids and glycerol in the same proportions as would be obtained from a mixture of butyrim, palmitin, and olein in the proportion of their molecular weights.

By treating butter with only half the quantity of alcoholic soda necessary for its complete saponification, and precipitating the liquid with water, Bell obtained an oil which solidified at  $44^{\circ}C$ , and on saponification yielded 88.1 per cent of insoluble acids, but no soluble fatty acids. This result agrees with the composition of an ester of the following character —



It is to be regretted that no determination of the glycerol was made.

The treatment of butter-fat with a proportion of alcoholic potash or soda insufficient for its complete saponification results in the formation of ethyl butyrate (butyric ether),  $C_4H_9 \ O \ C_4H_9O$ , and it has been shown by Fox and Wanklyn (*Analyst*, vii 73) that the quantity produced under favorable conditions corresponds to  $3\frac{1}{2}$  parts of butyric acid for 100 of butter-fat.

The fat from the butter of ewes' and goats' milk is very similar to that from cows' milk, but the esters of caproic and capric acids bear a larger proportion to the butyrim present than is the case with cows' butter.<sup>1</sup> The following figures by E. Schmitt show the relative composition of butter fat from the three sources —

<sup>1</sup> A sample of milk from the porpoise has been examined by Purdie, who found it to contain 45.8 per cent. of fat. A small quantity of this porpoise butter was, at his own request, submitted to the writer, who, on examining it by Reichert's method, obtained a distillate having an acidity corresponding to 1.57 per cent of valeric acid, which was proved to be the chief volatile fatty acid present. It is curious that the butter from the milk of a marine mammal should contain the ester of valeric acid,  $C_5H_{11}O_2$ , as its characteristic constituent, while in the butter from the milk of terrestrial mammals radicles of fatty acids containing an even number of carbon-atoms appear to be almost exclusively present.



	BUTTER-FAT FROM			
	Cows' Milk	Cows' Milk	Goats' Milk	Ewes' Milk
Melting point, °C (by method e, page 37)	36.5	36.5	33.5	37.5
Volatile and soluble fatty acids, per cent (in terms of butyric acid)	4.45	4.15	4.50	4.77
Fixed and insoluble fatty acids, per cent	88.57	89.15	84.40	85.25
" melting point	39.8	40.0	38.8	40.5

By long exposure to light, butter fat becomes completely bleached and notably altered in chemical composition. A specimen examined by P. Vieth gave 87.37 per cent. of insoluble fatty acids when fresh, while after exposure to diffused daylight for twelve months only 85.09 per cent. was obtained.

The peculiar characters and chemical composition of butter fat render its recognition easy. The subject is discussed at length in connection with the detection of adulterations of commercial butter.

The following are the results of examination of the mixed acids from butter-fat:—

Solidifying point,	33°–38° C	(Thoerner)
Melting point,	38°–45° C	
Saponification value		
(mgrm KHO),	210–220	(Thoerner)
Iodine value,	28–31.	(Thoerner.)
Heat of bromination,	6.2	(Hehner and Mitchell)
Refractive index,	1.437–1.439	(Thoerner)

## BUTTER

The general characters of butter are well known. It consists of a mixture of about 80 to 90 per cent. of butter-fat, with variable proportions of water, curd, and salt. Coloring matter is often added, and carbonate of sodium is sometimes employed to prevent rancidity.

In its ordinary state, butter readily becomes rancid, butyric acid being amongst the most prominent products of the change. Pure butter-fat is comparatively little liable to change.

Butter was formerly subject to numerous adulterations, some of which are of a very apocryphal nature. Starch, flour, soluble glass, &c, are among the doubtful sophistications. Lard, tallow, dripping, and other animal and vegetable fats were formerly extensively em-

ployed; but of late years by far the most extensive sophistication of butter has been an admixture with, or complete substitution by, the factitious butter now so largely manufactured and sold under the name "margarine." Excessive proportions of salt and water are occasionally met with, and coloring and flavoring ingredients are also used.

*Water* is best determined by placing 5 gm. or some other known weight of the butter in a small tared beaker, and exposing it in an air-bath to a temperature of  $105^{\circ}$  to  $110^{\circ}$  C until no more globules of water can be observed on looking at the beaker from below. The loss of weight undergone by the sample shows the amount of water in the quantity taken. Generally the water can be completely expelled in about one hour. The proportion of water normally present in butter is from 8 to 12 per cent. Sixteen per cent. may be regarded as the maximum proportion in good, well-made butter. James Bell, however, obtained from 117 samples of butter collected in various parts of the kingdom, and asserted by him to be genuine, proportions of water varying from 4.15 to 20.75 per cent., the mean of the whole being 14.2 per cent.

*Curd and salt* are most conveniently determined in the quantity of butter which has served for the estimation of the water. The fat is re-melted and filtered into a small tared beaker, kept in a warm place. The residual matter is rinsed on to the filter with petroleum spirit, redistilled at a temperature below  $80^{\circ}$  C, and washed with hot petroleum spirit till free from fat. The filter is then dried at  $100^{\circ}$  C, and the contents scraped off and weighed. After weighing, the residue, which represents the curd and salt of the butter, may be examined under the microscope for starch, cellular tissue, &c., and then, if desired, treated with cold water, and the solution further examined. Usually, however, it is sufficient to ignite the residue in porcelain at a low temperature, and regard the non-volatile matter as *salt*, the combustible as *curd*. It is evident that if a more minute examination be considered necessary, it will be well to operate on a larger quantity of the sample.

The proportion of salt normally present in butter varies from 0.5 to 5 or 6 per cent. Any higher proportion may be considered excessive, and to some extent suspicious. It is not possible to fix a limit for the amount of salt a sample of "fresh butter" should contain, as the proportion in butter called by that name varies considerably with the locality. The proportion of curd, except in rare cases, does not exceed 1 or 2 per cent.

*Fully matter* in butter may be determined indirectly by subtracting

the sum of the percentages of water, curd, and salt from 100.00. It may be estimated directly by evaporating off the petroleum spirit from the filtrate from the curd and salt, and adding the weight of the residual fat to that of the main quantity. It is not desirable to mix the filtrate and washings together, as the last traces of the solvent are volatilised with difficulty if the quantity of fat is considerable.

The official methods of the A. O. A. C. for the analysis of butter are as follows:—

*Preparation of the Sample*.—If large quantities of butter are to be sampled, a butter trier or sampler may be used. The portions thus drawn, about 500 gm., are to be perfectly melted in a closed vessel at as low a temperature as possible, and when melted the whole is to be shaken violently for some minutes till the mass is homogeneous and sufficiently solidified to prevent the separation of the water and fat. A portion is then poured into the vessel from which it is to be weighed for analysis, and should nearly or quite fill it. This sample should be kept in a cold place till analysed.

*Determination of the Water*.—From 1.5 to 2.5 gm. are dried to constant weight at the temperature of boiling water, in a dish with flat bottom, having a surface of at least 20 square centimetres. The use of clean, dry sand or asbestos with the butter is admissible, and is necessary if a dish with round bottom be employed.

*Determination of the Fat*.—The dry butter from the water determination is dissolved in the dish with absolute ether or with petroleum ether of 76°. The contents of the dish are then transferred to a weighed Gooch's crucible with the aid of a wash-bottle filled with the solvent, and are washed till free from fat. The crucible and contents are heated at the temperature of boiling water till the weight is constant. The weight of fat is calculated from the data obtained.

The fat may also be determined by drying the butter on asbestos or sand, and extracting by anhydrous alcohol free ether. After evaporation of the ether the extract is heated to constant weight at the temperature of boiling water and weighed.

*Determination of the Casein, Ash, and Chlorine*.—The crucible containing the residue from the fat determination is covered and heated, gently at first, gradually raising the temperature to just below redness. The cover may then be removed and the heat continued till the contents of the crucible are white. The loss in weight of the crucible and contents represents casein, and the residue in the crucible, mineral matter. In this mineral matter dissolved in water slightly acidulated with nitric acid, chlorine may be determined gravimetrically with silver nitrate, or, after neutralisation with calcium carbonate, volumetrically, using potassium chromate as indicator.

*Determination of the Salt*.—Weigh in a counterpoised beaker from 5 to 10 gms. of the butter. The butter is placed in portions of about 1 gm. at a time in the beaker, these portions being taken from different parts of the sample. Hot water (about 20 cc.) is now added to the beaker, and after the butter has melted, the liquid is poured into the bulb of a separating funnel. The stopper is inserted and the contents shaken for a few moments. After standing until

the fat has all collected on top of the water, the stop cock is opened and the water is allowed to run into an Erlenmeyer flask, being careful to let none of the fat-globules pass. Hot water is again added to the beaker, and the extraction is repeated from ten to fifteen times, using each time from 10 to 20 c.c. of water. The resulting washings contain all but a mere trace of the salt originally present in the butter. The chlorine is determined volumetrically in the filtrate by means of standard silver nitrate and potassium chromate indicator and calculated to sodium chloride.

The minimum limit formerly suggested by the Society of Public Analysts for the fat in butter was 80 per cent., thus allowing 20 per cent. for water, curd, and salt.

*Coloring matters* of various kinds are added to butter. Among the substances employed for the purpose, E. Schmitt enumerates mangelgold and carthamus flowers, saffron, carrot juice, and turmeric; more recently the coal-tar colors, coralline-yellow and victoria-yellow, are said to have been used, as also lead chromate. "Carottine" is apparently a solution of 1 part of annotta in 4 parts of oil, the annotta being partly replaced by turmeric for the lighter shades. "Orantia" is a solution of annotta and sodium carbonate in water.

Coal-tar colors, either Soudan I or closely analogous bodies, are now extensively employed as butter colors. They are insoluble in water, but freely soluble in fats.

For the detection of foreign coloring matters in butter, Martin's test will be found very satisfactory. Dissolve 2 parts of carbon disulphide in 15 parts of alcohol by adding the former in small portions and shaking gently. 25 c.c. of this mixture are placed in a convenient tube, 5 grm. of the butter-fat added, and the tube shaken. The carbon disulphide falls to the bottom, carrying with it the fatty matter, while any artificial coloring matter remains in the alcohol. The separation takes place in from one to three minutes. If the amount of coloring matter is small, more of the fat may be used. If the alcoholic solution be evaporated to dryness and the residue treated with concentrated sulphuric acid, annotta will be indicated by the production of a greenish-blue color. The production of a pink tint will indicate a coal-tar color of the Soudan group. The normal coloring matter of butter is not soluble in alcohol.

#### MARGARINE. DETECTION OF FOREIGN FATS IN BUTTER

As already stated, by far the most common adulteration of butter now practised is that of the addition of, or entire replacement of the true butter by, foreign fats. Formerly the sophistication consisted in actually incorporating with the butter more or less *lard*, *dripping*,

*tallow*, or similar fat, but of late years the adulteration has been generally conducted in a far more scientific and less objectionable manner.

Various *factitious butters* or *butter substitutes* are now extensively manufactured and sold under the names of oleomargarine, or margarine. The former is the legal title in the United States for all butter substitutes, the latter is the legal title in England and several other countries. For the manufacture of these factitious butters the fat is usually carefully selected, and brought to a proper consistency by removing the less fusible portion by hydraulic pressure, or increasing the proportion of olein by adding sesame, arachis, or cottonseed oil. The fat is then usually incorporated with milk and salt, and colored with annotta, &c, and sometimes more or less real butter is also added. A small amount of glucose is now often added. It is stated also, that butyric acid and certain butyrates have been employed in order to produce a still closer imitation of true butter. Among the fats known to be successfully employed are—the more fusible portions of mutton- and beef-fat, lard; cottonseed oil, sesame oil, arachis oil, palm oil, and purified coconut oil. Horse-fat, bone fat, and waste grease are also said to be used.

As a rule, the butter substitutes now manufactured are excellent imitations of butter and valuable articles of food. They differ, however, from real butter in certain important respects, and should not be sold without due acknowledgment of their nature.

The recognition of foreign fats in butter is dependent on the peculiar constitution of true butter-fat, and hence it is invariably necessary first to separate the water, curd, salt, &c., and obtain the fatty matter of the sample in a condition fit for further examination. For this purpose it is desirable to employ about 50 gm. of the sample. About this quantity should be placed in a dry beaker and exposed to a moderate temperature ( $50^{\circ}$  to  $60^{\circ}$  C.) until the whole has melted and the water and curd have settled to the bottom of the vessel. This will be induced more rapidly by careful stirring, so as to cause the curd to adhere to the sides of the beaker. The clear fat is then poured on a dry warm (ribbed) filter, and kept in a warm place until about 30 c.c. of filtrate are collected in a dry beaker. If the filtrate be not perfectly clear, it must be re-filtered after further careful heating. The fat should be kept as short a time as possible in a molten state, and the temperature should not be allowed to exceed  $70^{\circ}$  C., as otherwise the specific gravity and certain other characters of the fat may be seriously affected.<sup>1</sup>

<sup>1</sup> Inattention to the above essential conditions has led to serious errors. It was not improbably the cause of the Somerset House chemists declaring a sample to be genuine butter when the vendors had admitted the said sample to be factitious.

The fatty matter of the butter being thus isolated, its physical and chemical characters may be investigated.

Numerous methods of examining butter for foreign fats have been devised, but many are wholly worthless for their intended purpose unless the sophistication be of the gross character which is now almost obsolete. Thus the melting or solidifying point of the fat is no longer an indication of value, as margarine fat is carefully adjusted to about the same fusibility as butter. The observation of well-defined, double-refracting crystals under the microscope is now well understood to signify nothing but that the fat in question has undergone fusion and subsequent solidification.

The following is a description of those methods of examining butter for foreign fats which considerable experience has shown the author to be thoroughly reliable.—

The specific gravity of the molten fat is a valuable criterion of its nature. The test was originally suggested by James Bell, who showed that melted butter-fat was sensibly denser than lard and margarine. Bell took the specific gravity of the fat at 100° F. (37.8° C.), by means of a specific gravity bottle furnished with a thermometer, and his figures express the specific gravity of the fat at the temperature of the experiment compared with water at 100° F. Expressed in this way, the specific gravity of pure butter-fat was found by Muter to range from .9105 to .9138, being rarely below .9110. The author's experience of a large number of samples examined by this method practically confirms this result.

The following figures show specific gravities observed in butter-fat and its substitutes at a temperature of 100° F. (37.8° C.), water at the same temperature being taken as unity.—

	J BELL	J MUTER	A H ALLEN
Butter-fat.	.9094 to .9140	.9105 to .9138	.9099 to .9132
Margarine . . .	.9014 to .9038	.903 to .906	.902 to .905
Dripping . . .	.9040 to .9046	.904 to .907	
Lard . . .	.9038	.904 to .906	
Suet . . . . .	.9028 to .9037		

The determination of the specific gravity of fats at 100° F by means of a gravity-bottle may be advantageously replaced by the method suggested by C. Estcourt, who recommended that the determination should be made at the temperature of boiling water by means of a Westphal balance. The mode of operating employed by the writer

is fully described on pages 29 and 30 and leaves nothing to be desired. On reference to the tables on pages 31 and 32 it will be seen that melted palm oil, tallow, lard, and margarine are sensibly lighter than butter-fat, coconut oil, or cottonseed oil. The limits of specific gravity for butter-fat and margarine met with in practice are as follows —

Butter-fat,	867 to 870	} At 99° C
Margarine,	858.5 to 862.5	

The average specific gravity of butter-fat at 99° is 868, and that of margarine 861. Admixture of cottonseed oil will increase the specific gravity of margarine, but there is of course a practical limit to the employment of this as an ingredient of artificial butter. Coconut oil would readily raise the specific gravity of a sample to that of butter fat, but it would be detected on application of other tests.

It will be seen, therefore, that the determination of the specific gravity of the molten fat, if conducted under proper conditions, affords a useful indication of the purity of butter, and a means of roughly estimating the proportion of the foreign fat contained in adulterated samples.

By long-keeping, butter becomes so changed that the specific gravity of the fat is worthless as an indication of its purity.

Although the determination of the specific gravity of butter-fat is useful as a preliminary test, the indication, when taken alone, is not sufficiently reliable to justify the positive condemnation of a sample as adulterated, or even to prove it to be approximately genuine. For more definite information, the following methods must be employed —

The behavior of a sample of supposed butter-fat with glacial acetic acid (see also page 40) affords a valuable indication of its nature. It is simply necessary to pour 3 c c of the melted fat into a small test-tube, add an exactly equal measure of glacial acetic acid, and immerse the tube in boiling water, or heat the contents over a small flame till complete admixture takes place on agitation. The liquid is then allowed to cool spontaneously, while stirred with the bulb of a thermometer, and the temperature at which it becomes turbid is duly noted. A number of samples of butter-fat recently examined in the author's laboratory showed fairly corresponding turbidity-temperatures, the range for fifteen samples being only between 56° and 61.5° C. On the other hand, seven samples of margarine gave solutions in acetic acid which became turbid between 98° and 100° C.

A valuable method of examining butter-fat is the determination of the volatile fatty acids by Reichert's distillation process, as described

on page 58 As there stated, the value of its indications has been fully confirmed. There is no fat liable to be employed for the adulteration of butter which at all simulates the behavior of butter-fat when examined by Reichert's process<sup>1</sup> Even coconut oil, which resembles butter-fat in specific gravity, solubility in acetic acid, and saponification-equivalent, gives little more than one-fourth of the volatile and soluble fatty acids yielded by butter-fat If the absence of any considerable proportion of coconut oil is proved by the specific gravity of the sample not exceeding the limit for margarine, the proportion of foreign fat to butter-fat is indicated roughly by the results of Reichert's test Meissl's modification employing 5 grm of the fat has been very generally adopted, and the figures furnished by it are about 2 2 times the Reichert value

Considerable variation in the Reichert-Meissl value has been noted in the butter of different countries The lowest values are found in Italian butters, the minimum for which has been fixed at 20. In England, France, and Germany the minimum value has been fixed at 24, and in Sweden at 23

Values considerably below the limit of 24 have occasionally been found in English butters of known purity, thus, Vieth found figures from 20 4 to 21 4 in butter made from the milk of a particular English farm. Such low values are exceptional, and it is more usual to find them in the butter obtained from the milk of a single cow

If the Leffmann-Beam method of saponification be adopted, the figures are generally about 0 7 less than the above, due mainly to less interference of carbon dioxide.

The *saponification-equivalent* of butter-fat ranges from 241 to 253, the average being about 247. The figures for coconut and palmit oils vary between 209 and 228, while the usual other adulterants have equivalents exceeding 277 and averaging about 285

Although the careful examination of butter fat by the foregoing methods will almost invariably lead to the detection of any notable proportion of foreign fats, it is often important to obtain such further information as is afforded by determinations of the relative proportions of soluble and insoluble fatty acids yielded on saponification. As stated on page 45 *et seq.*, ordinary fats, consisting of mixtures of palmitin, stearin, and olein, yield on saponification fully 95 per cent of fatty acids, of which all but a small fraction will be insoluble in

<sup>1</sup> *Butyric acid and artificial butyric*, suspected to be sometimes added to butter-substitutes, might be detected by treating the fat with a limited quantity of alcohol, and examining the resultant solution by Reichert's method



water. Butter fat, on the other hand, owing to its containing radicals of butyric and other of the lower fatty acids, yields on saponification fatty acids which consist to a notable extent of butyric acid and other fatty acids soluble in water. The fatty acids insoluble in water range from 86.5 to about 89 parts for every 100 of butter-fat taken, while the soluble fatty acids, as determined by their neutralising power, range from 4.5 to nearly 7 per cent. Associated with the butyric acid are higher homologues, such as caproic acid, having a very limited solubility in water, and therefore only separated with difficulty from the true insoluble acids. Therefore, if the amount of soluble fatty acids be determined by titrating the aqueous solution with standard alkali, the volume of normal solution required being calculated to its equivalent of butyric acid, the result obtained is below the true amount, owing to the caproic acid, &c., being regarded as butyric acid, which latter acid has a lower combining weight. This fact may be borne in mind, but has no practical influence on the results.

The examination of butter-fat by the determination of the insoluble fatty acids was first suggested by Messrs. Angell and Hehner, but the original process has been greatly improved by Turner, Jones, and other chemists, and by Muter, who devised a process for determining the soluble fatty acids. The following details of operating are those which in the author's experience are most satisfactory. The utmost care is necessary throughout the analysis —

Before commencing the operation, the following standard solutions must be prepared. —

(a) Dissolve 14 grm. of good stick-potash in 500 c.c. of rectified spirit, or methylated spirit which has been redistilled with caustic alkali, and allow the liquid to stand till clear. This solution will be approximately seminormal.

(b) A standard hydrochloric or sulphuric acid of approximately seminormal strength.

(c) Accurately prepared decinormal sodium hydroxide. Each 10 c.c. contains .0040 grm. of NaHO, and neutralises .0085 grm. of butyric acid,  $C_4H_7O_2$ .

A quantity of the butter-fat (separated from water, curd, and salt, as described on page 185) is melted in a small beaker, a small glass rod introduced, and the whole allowed to cool and then weighed. It is re-melted, stirred thoroughly, and about 5 grm. poured into a strong 200 c.c. bottle. The exact weight of fat taken is ascertained by re-weighing the beaker containing the residual fat.

By means of a fast delivering pipette, 50 c.c. measure of the alcoholic

potash (solution *a*) is run into the bottle, and the pipette drained exactly 30 seconds. At the same time, another quantity of 50 c.c is measured off in an exactly similar manner into an empty flask.

The bottle is fitted with an india-rubber stopper, which is tightly wired down, and is placed in the water-oven, and from time to time removed and agitated, avoiding contact between the liquid and the stopper. In about half an hour, the liquid will appear perfectly homogeneous, and when this is the case the saponification is complete and the bottle may be removed. When sufficiently cool, the stopper is removed and the contents of the bottle rinsed with boiling water into a flask of about 250 c.c capacity, which is placed over a steam bath, together with the flask containing merely alcoholic potash, until the alcohol has evaporated.

Into each of the two flasks is now run about 1 c.c more seminormal acid (solution *b*) than is required to neutralise the alkali, and the quantity used accurately noted. The flask containing the decomposed butter-fat is nearly filled with boiling water, a cork with a long upright tube fitted to it, and the whole allowed to stand on the water-bath until the separated fatty acids form a clear stratum on the surface of the liquid. When this occurs, the flask and contents are allowed to become perfectly cold.

Meanwhile, the blank experiment is completed by carefully titrating the contents of the flask with the decinormal soda, a few drops of an alcoholic solution of phenolphthalein being added to indicate the point of neutrality.

The fatty acids having quite solidified, the resultant cake is detached by gently agitating the flask, so as to allow the liquid to be poured out, but avoiding fracture of the cake. The liquid is passed through a filter to catch any flakes of fatty acid, and is collected in a capacious flask. If any genuine butter be contained in the sample, the filtrate will have a marked odor of butyric acid, especially on warming.

*Boiling* water is next poured into the flask containing the fatty acids, a cork and long glass tube attached, and the liquid cautiously heated till it begins to boil, when the flask is removed and strongly agitated till the melted fatty acids form a sort of emulsion with the water. When the fatty acids have again separated as an oily layer, the contents of the flask should be thoroughly cooled, the cake of fatty acids detached, and the liquid filtered as before. This process of alternate washing in the flask by agitation with boiling water, followed by cooling, and filtration of the wash-water, is repeated three times, the washings being added to the first filtrate. It is often difficult to get

the washings free from acid, but when the operation is judged to be complete, the washings may be collected separately and titrated with decinormal soda. If the amount required for neutralisation does not exceed 0.2 c.c., further washing of the fatty acids is unnecessary.

The mixed washings and filtrate are next made up to 1000 c.c., or some other definite measure, and an aliquot part carefully titrated with decinormal soda (solution c). The volume required is calculated to the whole liquid. The number so obtained represents the measure of decinormal soda neutralised by the soluble fatty acids of the butter fat taken, *plus* that corresponding to the excess of standard acid used. This last will have been previously ascertained by the blank experiment. The amount of soda employed in this is deducted from the total amount required by the butter-fat quantity, when the difference is the number of cubic centimetres of standard soda corresponding to the soluble fatty acids. This volume multiplied by the factor 0.0088 gives the butyric acid in the weight of butter fat employed.

The flask containing the cake of insoluble fatty acids is thoroughly drained and then placed on the water-bath to melt the contents, which are poured as completely as possible into the (wet) filter through which the aqueous liquid was previously passed. The fatty acids are then washed on the filter with boiling water to remove the last traces of sparingly soluble acids. The filter is then placed in a small dry beaker and treated in the manner described on page 51, the main quantity of fatty acids and the supplementary portion subsequently dissolved out of the flask and filter being weighed separately.

When it is only required to determine the insoluble acids of butter-fat, the foregoing tedious mode of operating may be avoided by diluting the soap solution obtained by saponifying 5 grm. of the fat till it measures about 300 c.c. The large excess of alkali is then neutralised by cautious addition of hydrochloric acid, and the hot solution treated with a slight excess of barium chloride or magnesium sulphate. The precipitated barium or magnesium soap is well washed with hot water, and then rinsed off the filter into a separator, where it is decomposed by dilute hydrochloric acid. The resultant layer of insoluble fatty acids is washed by agitation several times with warm water, and is then treated as directed on page 51.

In the analysis of butter-fat, the sum of the insoluble fatty acids by weight and of the soluble fatty acids calculated as butyric acid should always amount to *fully* 94 per cent. of the fat taken. In the author's own experience, the sum more frequently approaches or even exceeds 95 per cent., especially if the butter be adulterated.

The soluble fatty acids, calculated as butyric acid, should amount to at least 5 per cent., any notably smaller proportion being probably due to adulteration. The insoluble fatty acids from genuine butter-fat rarely exceed 88.5 per cent., occasionally reaching 89 per cent., but a sample ought scarcely to be regarded as certainly adulterated unless the insoluble acids exceed 89.5 per cent. As a standard for calculation, 88 per cent. of insoluble acids may be regarded as a fair average, the soluble acids being taken at 5.5 per cent.

By long keeping, butter undergoes change in a very variable manner. Thus, when butter-fat is kept exposed to light for a long time, the proportion of insoluble fatty acids is decreased (see page 181), but when ordinary butter is kept, more or less fermentation occurs with development of fungi. With some samples the change is very slight, while in other cases the butter loses its characteristics, and the composition of the fat is more or less changed, the percentage of insoluble acids being increased. The following figures are due to J. Bell.—

Insoluble acids, original butter, . . .	87.90	87.80	85.50	87.40	87.72	87.63
„ after keeping, . . .	88.87	90.00	85.72	87.07	88.10	88.00
„ difference, . . .	1.67	2.20	0.22	0.67	0.68	0.35
Length of time kept, in weeks, . . .	12	7	7	6	8	6

The upper part of a sample of butter, kept for six years in an opaque, loosely-closed jar, was found by Vieth to be extensively attacked by fungi, and to yield 90.9 per cent. of insoluble fatty acids.

Tallow, lard, and most vegetable oils contain distinct traces of substances yielding soluble fatty acids on saponification, the proportions present corresponding to 0.1 to 0.5 per cent. of butyric acid; while coconut and palmnut oils yield notable quantities of soluble or volatile fatty acids. The acids of coconut oil soluble in water are chiefly caproic and capric, and hence if the neutralised solution of the fatty acids be concentrated, acidulated, distilled, and the distillate neutralised by barium hydroxide (see page 50), the barium salts obtained will have a composition pointing to a notably higher combining weight for the soluble fatty acids than when butter-fat is similarly treated.

The bromine- and iodine-absorptions of butter-fat differ materially from the corresponding figures for margarine, but the distinction is not so sharp as in the case of the processes already described. A judiciously made mixture of coconut oil and animal fat would give an iodine- or bromine-absorption similar to that of butter-fat.

Considerable use is made of refractometric examination of butter,

especially for the rapid sorting of numbers of samples. Various forms of instruments are employed, but the indications furnished by all of these must be checked by other methods.

Amagat and Jean's oleo-refractometer and Zeiss' butyro-refractometer have found most favor by reason of their handiness and the facility in the manipulation entailed.

Jean prepares the sample for examination in the oleo-refractometer as follows: Melt from 25 to 30 grm of butter in a porcelain dish at a temperature not exceeding 50° C.; stir well with a pinch or two of gypsum and allow to settle out at the same temperature. Then decant the supernatant fat through a hot-water funnel plugged with cotton-wool, and pour it while warm into the prism of the apparatus. Stir with the thermometer until the fat has cooled to 45° C, and observe the deviation. Ether must not be used for the solvent, as minute traces of it seriously influence the result.

Genuine butter usually gives a deviation of 29 to 31. Pearmain has found in fifteen samples a maximum of 34 and a minimum of 25. The following are some observations made by Jean and Pearmain —

FAT	DEGREES	OBSERVER
Margarine, No 1	-13 to -18	Pearmain
"    No 2	-17	Jean
Butter with 10 per cent of No 2	-25	"
"    "    20	-26	"
"    "    30	-25	"
"    "    50	-23	"
Cotton seed oil	-20	"
Neutral coconut oil	-50	"
Lard	-8 to -14	Pearmain
Tallow	-15 to -18	"
Cottonseed oil	+17 to +23	"
Arachis oil	+5 to +7	"

De Bruyn has observed deviation as low as -21 in butters having the normal amount of volatile fatty acids. Jean states that such abnormal values were found only when the cow had been fed upon linseed cake.

A similar cause of error arises from the fact that the coloring matter added to butter is sometimes dissolved in a small quantity of cottonseed or other vegetable oil. It must be borne in mind, also, that a mixture of margarine and coconut oil may be prepared, having exactly the same deviation as that of genuine butter.

It is evident, from a study of the data furnished by the foregoing methods, that the Reichert process is by far the most reliable means of detecting adulteration. In cases in which the Reichert-Meißl

value does not exceed the lowest limit of 24, it is difficult and usually impossible to determine with certainty whether the sample is or is not adulterated. Determination of the saponification number and specific gravity and examination in the oleo-refractometer may aid in some instances.

### Neatsfoot Oil.

(See also page 98.) Neatsfoot oil is obtained by boiling the feet of oxen in water till all the oil rises to the surface. The commercial oil is often prepared from the feet of sheep and horses. Neatsfoot oil is yellow, odorless, and of bland taste. It deposits solid fat on standing. It does not readily become rancid and is highly esteemed for lubricating. It is largely adulterated with bone oil, fish, seed and mineral oils. The specific gravity at  $15.5^{\circ}$  usually ranges from .914 to .916, some samples prepared by Coste and Parry (see below) gave slighter higher figures. Taken at  $98^{\circ}$ – $99^{\circ}$  C. and compared to water at  $15.5^{\circ}$  a sample examined by the author had a specific gravity of .8619. The iodine number of neatsfoot oil ranges from 66 to 72, and its determination will often aid in detecting adulteration. The use in temperature with sulphuric acid is also of value for the same purpose, Jean observed a rise of  $77^{\circ}$ – $78^{\circ}$  (see also below). Mineral oils are detected by a determination of the unsaponifiable matter. The following are some results obtained by T. H. Coste and E. J. Parry from the examination of two samples of oil prepared in the laboratory.—

	I.	II
Specific gravity $\frac{15.5^{\circ}}{15.5^{\circ}}$ . . .	.9169	.9174
Temperature rise and sulphuric acid (equal vols.)	$58^{\circ}$	$56^{\circ}$
Viscosity at $110^{\circ}$ F (Redwood's) .	70 sec	
" " $200^{\circ}$ F (viscosimeter)	43 sec	
Iodine number . . .	71.1	72.4
Percentage of KHO for saponification .	19.60	19.71
Free acid (KHO required) . . .	trace	0.07
Insoluble fatty acids (Hchner's method)	95.3	95.5

The mixed fatty acids from the above gave the following figures.—

	I	II
Specific gravity $\frac{100^{\circ}}{100^{\circ}}$ . . .	.8742	.8800
Iodine number . . .	745	758
Percentage of KHO for neutralisation .	20.12	20.06
Mean combining weight . . .	270	280
Melting point . . . . .	29.2	28.5

The solidifying point (titer test) of a sample examined by Lowitsch was 26.1–26.5°

### Egg Oil.

The oil of egg is obtained from the yolk of hard-boiled eggs either by pressure or by solvents. Data have been furnished by several observers. Column A shows the results obtained by Paladino and Toso (*Analyst*, 1896, 161) from the oil extracted by moderate heating and pressure. Results in column B were given by Kitt from oil obtained by ether-extraction —

	A	B
Specific gravity,	0.9156 (at 20°)	0.9144 (at 15°)
Saponification-equivalent,	300–303	294.9 (mean)
Iodine number,	81.2–81.6	72.1
Reichert-Meißl number,		0.4
Glycerol, per cent,		10.4
Cholesterol, per cent,		1.6
Melting point,	22.0°–22.5°	
Solidifying point,	8.0°–10.0°	

### MIXED FATTY ACIDS

Melting point, . . .	34.5°–35.0°	36.0°–39.0°
Saponification number (mean), . .		194.9
Iodine number (mean), .		73.7

### Codliver Oil.

*French*—Huile de foie de morue    *German*—Leberthran.

(See also pages 100 and 122.) Strictly speaking, codliver oil is the oil obtained from the liver of the cod, *Gadus morrhua*. Other species of *Gadus* and of the *Gadidae* family, such as the ling, cod-fish, dorse, hake, haddock, and whiting, yield a closely analogous oil.

Several qualities of codliver oil are recognised in commerce:—pale, used only in medicine; light brown, an after-yield, of inferior quality, but still largely used in medicine, and dark brown, or tanners' oil, obtained by roughly boiling down the livers remaining from the foregoing processes.

The purest codliver oil has a pale yellow color, and is never quite colorless unless artificially bleached. It is limpid, has a slight odor and taste, and a faint acid reaction. If prepared at a high temperature, or if the livers be allowed to partially putrefy, the acid reaction is more decided and the color pale or dark brown, the darkest varieties being transparent only in thin layers, and having a repulsive, fishy odor, and bitterish acid taste.

The following are the physical characteristics of different qualities of codliver oil, according to DeJongh:—

	1ST QUALITY	2ND QUALITY	3RD QUALITY
Color	Golden yellow	Pale brown	Dark brown, greenish by transmitted light
Specific gravity at 17.5° C	923	924	920
Behavior when cooled to -13° C	Deposits solid fat	..	Deposits no solid fat
Parts of absolute alcohol required for solution	40	31-36	17-20
" " " Boiling	22-30	13	17-20

The composition of codliver oil is very complex. Olein appears to be absent. Besides palmitin and stearin, Heyerdahl noted the presence of 20 per cent. of jecothic acid and 20 per cent. of therapeutic acid. The author has also observed the presence of a sensible quantity of cholesterol and of volatile fatty acids. The latter, however, appear to be secondary products, due to putrefactive changes in the livers. The best oils prepared by the use of steam are free from volatile acids. Gaduic acid was obtained by Luck from the deposit from a light-brown oil, and, when recrystallised from hot alcohol, melted between 63° and 64°.

The following bases have been isolated from codliver oil: butylamine, isoamylamine, hexylamine, dehydrolutidine, morrhaine, and aselline. Trimethylamine, derived probably from the decomposition of the liver tissue, has also been detected.

The presence of biliary compounds, as stated by earlier investigators, is now denied.

Codliver oil contains traces of iodine, and sometimes of bromine, but the form in which these elements exists is unknown. The proportion of iodine, judging from the statements of different investigators, is very variable. The question has been reinvestigated by E. C. Stanford, who found the proportion of iodine to be extremely minute, ranging from 138 to 484 mgm. per 100 gm., with an average of 322. The proportion in the flesh of dry cod-fish and herrings is considerably larger than in codliver oil. It is impossible to attribute the medicinal value of codliver oil to the trace of iodine present, its chief recommendation for medicinal use is probably the facility with which it is digested and assimilated.



The following are analytical results obtained from the mixed fatty acids of codliver oil —

Solidifying point (titer test),		
Medicinal,	17.5°–18.4° C	(Lewkowitsch)
Coast cod,	18.7°–19.3°	"
Norwegian,	13.3°–13.9°	"
Dark unripped,	22.5°–24.3°	"
Melting point,	21°–25°	(Parry and Sage)
Saponification value		
(mgm KHO),	204–207	
Iodine value,	130–170	
Refractive index,	1.4521	(Thoerner)

#### EXAMINATION OF CODLIVER OIL

Codliver oil to which iodine or compounds of iodine have been purposely added is now employed in medicine. These additions are dissolved on agitating the oil with alcohol, and can be detected in the spirituous solution by the usual tests. The ash left on igniting natural codliver oil contains no trace of iodine, but if an iodide has been added it will be found in the incombustible residue. The usual proportion of iodine in iodised codliver oil is about 0.1 per cent.

A ferrated codliver oil is also employed, containing about 1 per cent of ferrous oleate.

Good medicinal codliver oil should deposit no stearin at 0° C. (*Pharm. Germ.*), but a granular crystalline deposit is often produced on cooling oils of the lower qualities.

The *British Pharmacopoeia* describes codliver oil as pale yellow, with a slight fishy odor, and a bland, fishy taste. It states that it is the oil extracted from the fresh liver of the cod, *Gadus morrhua*, without giving any test by which it can be distinguished from allied oils.

As previously stated, the "codliver oil" of commerce is in practice obtained from several members of the *Gadidae*, or cod family; and, as long as it is produced from these fish solely, little exception can be taken. The livers of various other fish are, however, apt to be employed, and the detection of the substitution is very difficult.

According to Salkowski, a good codliver oil should not have a higher Reichert value than 0.20. A higher figure would indicate that the oil had been prepared from livers that had undergone putrefaction. The iodine absorption is also a useful criterion of the quality of a codliver oil, those obtained from decayed livers showing lower values.

OIL	SPECIFIC GRAVITY AT 15.5° C	COLORATION WITH NITRO-SULPHURIC ACID	
		Before stirring	After stirring
Cod-liver	9290	Violet, quickly becoming rose-red	Rose-red, changing to light brown
Hake-liver	9270	Dark violet, changing to dark brown	Brownish violet, changing to light brown
Skate-liver	9327	Light violet, changing to brown	Brownish violet changing to brown
Shark-liver	9285	Light brown, with spots of red	Light brown, becoming darker
Herring	9326	Brown	Darker brown
Sprat	9284	Light brown	Unchanged
Seal	9245	Light brown	Lemon-yellow, rapidly changing to emerald-green and bluish green
Whale	9301	Light brown	Darker

The specific gravity of cod-liver oil varies from .922 to .930 at 15.5°, the darker varieties being generally the heaviest. The oil from fish allied to the cod is sometimes of a slightly higher specific gravity. Thus, that prepared in Grimsby from a mixture of the livers of cod, haddock, ling, and whiting, has a specific gravity of .930, while the product obtained in Aberdeen from haddock livers has a specific gravity of .931, is somewhat less viscous, and develops more heat with sulphuric acid than the other varieties of cod-liver oil.

Samples of cod-liver and other fish oils prepared by the Normal Company, Aberdeen, were found in the author's laboratory to have the specific gravities stated in the table on the preceding page, and to give the colorations described when two drops of a mixture of equal measures of concentrated sulphuric and nitric acids were added to 20 drops of the oil, on a white surface. From the figures it is evident that the specific gravity affords no reliable indication of the presence of other fish oils in cod-liver oil.

Cod-liver oil is remarkable for the great increase of temperature produced by treating it with sulphuric acid (page 77), and for its high iodine-absorption. These characters distinguish it from most other oils except liver oils.

Cod-liver oil gives a fine violet coloration, or a dark red spot with violet streaks, when treated with strong sulphuric acid as described on page 85. The color subsequently changes to reddish brown. The reaction is distinctly produced by cod-liver oil, but is common, with modifications, to all liver oils.

For the detection of other *liver oils* in codliver oil, M Boudard employs pure fuming nitric acid, which is said to produce a beautiful rose-red coloration with pure oils, but not with mixed oils. H Meyer proposes to distinguish the oil from the liver of the true cod from that yielded by allied fishes by mixing 10 parts of the sample with 1 of a mixture of equal parts of strong sulphuric and nitric acids (compare table on page 196). Codliver oil turns a fiery rose, changing quickly to a lemon-yellow. The oil from the "haakjaerring" also turns to a rose, but changes to a brownish violet. The oils from other *Gadidae* give a yellow color of less pure tone than is yielded by true cod oil. Oil from the French roach gives a chestnut-brown coloration, while the oil from the Mediterranean roach turns a dark violet. M Cailletet employs a mixture of 12 parts of phosphoric acid of 1.44, 7 of strong sulphuric acid of 1.84, and 10 of nitric acid of 1.37 specific gravity, 1 c.c. of this mixture is agitated for some seconds with 5 c.c. of the oil, and then 5 c.c. of petroleum spirit added to dissolve the oil. Codliver oil shows after twenty-four hours a well-defined yellow color. All other fish oils give a marked brown tint, except *ray liver oil*, which invariably takes a red color. The last-named adulterant is said to be very common, and is difficult of detection.

Excessive amount of unsaponifiable matter may point to adulteration either by mineral oil or shark-liver oil.

Refined *seal oil* has been extensively used as an adulterant of cod liver oil. According to J. L. Rossler, codliver oil gives with aqua-regia a dark greenish-yellow liniment, which becomes brown in half an hour, while white seal oil, or a mixture of equal parts of seal and cod oils, gives merely a pale yellow liniment. The presence of seal oil may be inferred from the altered figures obtained on determining the saponification-equivalent, bromine-absorption, and rise of temperature with sulphuric acid. A factitious codliver oil, composed of 30 per cent of white seal oil and 70 per cent. of Japanese fish oil, has been described by Krieger.

Most *seed oils* can be detected in codliver oil by their peculiar absorption spectra, the spectrum of codliver oil being almost identical with that of almond oil. Almond oil itself, as also the more probable adulterant, *lard oil*, would be detected by the diminished specific gravity and iodine-absorption of the sample, and by its altered behavior with sulphuric and nitrous acids.

**RAY LIVER OIL**, obtained from the *Raja batis*, has been proposed as a substitute for codliver oil. It is bright or golden yellow in color, has a specific gravity of .928, is neutral in reaction, and has a slightly

fishy odor and taste. It darkens but little under the influence of chlorine, and is said to give an odor of valeric acid when heated with a solution of caustic alkali.

#### Shark-liver Oil. Shark Oil.

*French*—Huile de requin *German*—Haifischöl, Haileberthran.

(See also pages 100 and 122) The shark oil known in commerce is chiefly obtained from the liver of the basking shark or sunfish (*Squalus marinus*), chiefly caught off the coast of Norway, but the dogfish and several allied fish also contribute to it.

Shark oil has been largely employed in tanneries and as a substitute for codliver oil, but in England it is now almost disused.

Owing to frequent adulteration, the physical and chemical characters of shark oil have been misstated by many authorities. Thus it is commonly alleged to be of very low specific gravity, a character in all probability really due to the presence of a large proportion of mineral oil or similar adulterant, which addition caused the saponified sample to yield large ether-residue (page 114). Whether or not these oils of low specific gravity were uniformly adulterated is no longer of much practical interest, as oil of such character is not now to be met with. The "shark oil" usually indicated 40° to 42° on Casartelli's oleometer, and the analogous "African fish oil" 48° to 50° (see footnote, p. 204).

The author has examined a number of specimens of shark-liver oil which there is reason to believe genuine. Whilst throwing doubt on older statements, the results show that shark oil is peculiar in yielding a very notable proportion of unsaponifiable matter, consisting in great part of cholesterol. If the sample be saponified in the usual way, and the aqueous solution of the soap agitated with ether, the separated ethereal layer leaves on evaporation a nearly colorless crystalline mass, which, if dissolved in boiling alcohol, deposits abundant plates of cholesterol, which yield the characteristic color-reactions.

The following results were obtained in the author's laboratory by the analysis of six specimens of apparently genuine shark-liver oil —

	1 JAPANESE	2 CHINA	3 RUSSIAN	4	5	6
Specific gravity at 15.5° C	0.9260	0.9185	0.9285	0.9143	0.9136	0.9113
Percentage of KHO required	17.73	16.96	19.76	15.3	11.0	11.0
=Saponification-equivalent	316.4	330.8	283.9	160.9	400.0	400.0
Ether-residue, per cent.	2.82	8.70	0.70	10.25	17.30	10.31

With concentrated sulphuric acid Nos. 1 and 3 samples gave a reddish-brown spot with violet edges, the whole changing on stirring to reddish brown. Nos. 2, 4, 5, and 6 agreed in giving a bright-violet spot changing to blood-red; on stirring, the whole became a magnificent violet color, changing rapidly to dark red and brown.

The ether-residues from these samples, varying from 0.7 to 17.3 per cent, were highly crystalline, and chiefly composed of cholesterol. The variations in the specific gravity of the samples follow closely the proportions of ether-residue. If the percentage of potash be calculated on 100 parts of the oil actually saponified, and not on 100 parts of the sample including the unsaponifiable matter, the proportion is found to range from 17.0 to 19.6 per cent, and the corresponding saponification-equivalents from 330 to about 282.

It is of interest to compare these results with those obtained by the analysis of samples of presumably adulterated shark oil:—

	A	B	C	ATLANTIC FISH OIL
Specific gravity at 15.5° C.	8746	8692	8661	8672
Percentage of KHO required		4.50	5.50	
Ether-residue	80.9	80.8	83.5	82.5

The ether-residue was generally of a bright-yellow color like the original oil, remained quite clear on cooling, and volatilised somewhat readily. A further examination was made of the ether-residue from sample B, which was free from nitrogen and nearly free from oxygen. It gave when heated an unmistakable odor of pine resin; and appeared to be a mixture of light rosin oil with shale or petroleum lubricating oil. With concentrated sulphuric acid, B gave a reddish-brown coloration, becoming darker on stirring.

#### Whale Oil. Train Oil.

*French*—Huile de baleine. *German*—Thran

(See also pages 100 and 122.) The product known in commerce as whale oil is derived from the blubber of various members of the whale tribe. The Greenland or "right" whale (*Balaena mysticetus*) is the chief of these. It inhabits the polar seas of both hemispheres, and yields the product properly termed "train oil," though that term is now extended to the oil from the blubber of any marine mammals, including seals. The polar whale (*B. glacialis*), the humpback whale (*Balenoptera boops*), and the finner (*Balenoptera Gibbar*) also inhabit

the northern seas, while the Cape whale (*Balæna antarctica*), the black whale (*Balæna australis*), and a number of allied species are found in the southern. The oils from the different species of porpoise present a strong resemblance to ordinary whale oil, while, on the other hand, the oils from the cachelot and dogling, and probably from other toothed cetaceans, are essentially different both in their chemical constitution and practical applications, and hence are described in another section (page 204). The oil is usually extracted by boiling the blubber with water, and skimming the oil from the aqueous liquid and refuse tissue.

Whale oil is ordinarily a brown or brownish-yellow liquid, having a marked and offensive "fishy" smell and taste, but by suitable treatment these peculiarities can be greatly reduced. When subjected to cold some varieties of whale oil readily deposit palmitin, which is sometimes used for soap making, though the odor of the product indicates its origin.

The chemical constitution of whale oil is very variable. Some varieties, especially the southern product known in commerce as Bahia whale oil, exhibit strongly-marked drying properties. Some specimens of whale oil are nearly free from esters of lower fatty acids, while in others these are present in very notable proportion. The most characteristic and abundant of these is valerin, and the very variable proportion which may be present is indicated by the figures on page 59, showing the behavior of the saponified oil when acidulated and distilled. Other figures indicating the comparative constitution of the oils from marine mammals are given on page 122.

Observations on the mixed fatty acids of whale oil have been made as follows —

Specific gravity at 100° C (water at 100° = 1),	8922	(Archbutt)
Solidifying point (titr test),	22 9°-23 9°	(Lewkowitsch)
Melting point,	27°	(Jean)
" "	14°-18°	(Schwentzer and Lungwitz)
Iodine absorption,	130 3-133	" "

Whale oil is little liable to adulteration, except with seal oil and hydrocarbon oils, the presence of hydrocarbon oil can be detected and the proportion determined as described on page 112.

### Porpoise Oil.

*French*—Huile de marsouin. *German*—Meerschweinöl

(See also pages 100 and 122) Commercial porpoise oil is derived not only from the black porpoise (*Delphinus phocaena*), usually caught

off the coast of Denmark and in the Mediterranean and Black Sea near Trebizond, but also largely from the white whale (*Beluga catodon*), caught in the White Sea, the St. Lawrence, and on various parts of the Canadian coast. The oils from the *grampus* (*Phocaena orca*) and the various species known as black fish, especially *Globicephalus macrorhynchus*, also rank as "porpoise oil."

Porpoise oil is prepared in much the same manner as whale oil. In some instances, oil of a superior quality drains from the blubber at the ordinary temperature, but the greater part is obtained by boiling the tissue with water. In the case of the cetacean last named a very fine, limpid product termed "melon oil," used for lubricating delicate mechanisms, is obtained from the head. It is probably analogous to sperm oil.

Porpoise oil presents a general resemblance to whale oil, but is usually less offensive. It has considerable drying tendencies, and by keeping and exposure increases notably in specific gravity. A sample examined by the author had originally a specific gravity of .920, but after keeping for three years two portions of the same oil preserved under different conditions had respective specific gravities of .926 and .932.

Porpoise oil is remarkable for containing a considerable proportion of valerin. A sample examined in the author's laboratory yielded 5.06 per cent. of volatile fatty acids, having a mean combining weight of 104.7 ( $C_6H_{10}O_2 = 102$ ). Chevreul, who was the original discoverer of valeric acid, which he isolated from porpoise oil and called "phoenicic acid," prepared barium salts of volatile fatty acids equivalent to 9.63 per cent. of valeric acid, so that the composition of the oil is evidently very variable. From a sample of dolphin oil (from *Delphinus globiceps*), Chevreul prepared barium salts corresponding to 20.6 per cent. of valeric acid, besides a considerable proportion of spermaceti. Hence dolphin oil appears to be intermediate in composition between sperm oil and porpoise oil.

Owing to its peculiarity of constitution, porpoise oil has a low saponification-equivalent (255-256) and gives a very acid distillate by Reichert's test (page 59). It is saponified with great facility even by aqueous potash, the product being colored reddish brown. With the elaidin-test porpoise oil gives but little solid elaidin. Other characters are given on page 100.

Moore obtained a Reichert value of 56 and Steinbuch a Reichert-Meissl value of 131.6 for *porpoise-jaw oil*. Samples of porpoise-jaw oil also gave iodine absorptions of from 30.9 to 76.8 per cent.

### Sperm Oil.

*French*—Huile de cachelot. *German*—Wallrathol

(See also pages 101 and 122) Sperm oil proper is obtained from the head-cavities and blubber of the cachelot or sperm whale (*Physeter macrocephalus*). Several other of the toothed whales yield allied products, and the oil from one of these, namely, the dægling, or bottlenose whale, is known under the name of "Arctic sperm oil."

Sperm oil on cooling readily deposits crystalline scales of spermaceti. This is removed by filtration, but unless the operation be conducted at a very low temperature a portion of the wax is liable to remain in solution.

Sperm oil is a thin yellow liquid, and when of good quality is nearly free from odor. Inferior specimens have an unpleasant fishy smell and taste. Its specific gravity is very low, ranging between .875 and .884 at 15.5° C.<sup>1</sup>

Sperm oil is one of the most valuable oils in commerce. It has been found preferable to any other oil for lubricating the spindles of cotton and woollen mills, and for light machinery generally.

Sperm oil owes its value as a lubricant largely to its having little or no tendency to gum or become rancid, and to the comparatively slight change in viscosity produced by an increase of temperature.

If the oils from the allied toothed cetaceans be excepted, sperm oil has a unique constitution, since it consists essentially of esters of higher members of the methyl series.

Some indication of the peculiar composition of sperm oil was given in 1823 by Chevreul. Chevreul's observation seems to have been wholly forgotten until the author some years since called attention to the unique constitution of sperm oil.

Sperm oil gives on saponification products very different from those yielded by ordinary oils. When saponified with potassium hydroxide it forms potassium oleate and dodecetyl alcohol and some allied bodies. By agitating the aqueous solution of the resultant soap with ether, the higher alcohols are dissolved, and may be recovered by evaporating the solvent. The fatty acids may be isolated by acidulating the soap solution. Very little glycerol can be isolated after saponification, though the presence of a small proportion is indicated by the permanganate method.

<sup>1</sup> Dealers in sperm and similar oils commonly use a special hydrometer, devised by Casartelli, on the scale of which water is 0°, and rape oil 28°. Sperm oil stands at 44° to 46° and southern whale oil at about 24° on the same scale.



The higher alcohols, isolated in the above manner, form a pale yellow solid semi-crystalline substance, the melting point of which depends on the completeness with which the oil had been previously purified from spermaceti. They are insoluble in water, but readily soluble in alcohol and ether, and are volatile apparently without change in a vacuum, condensing as a perfectly colorless liquid, of .830 specific gravity at 100° C, which solidifies on cooling to a crystalline mass. The ether-residue from sperm oil is apparently a mixture of homologous alcohols, some specimens having given the author, on combustion, figures corresponding approximately to the formula  $C_{15}H_{34}O$ , and others to  $C_{12}H_{22}O$ . Probably both these alcohols, together with varying proportions of their homologues, are actually present.

The fatty acids from sperm oil have all the characters of an acid of the oleic series mixed with one of the stearic series. They are liquid, or nearly so, when cold, have a specific gravity of .899 at 15.5° C., are readily solidified by nitrous acid, and have a mean combining weight ranging from 281 to 294.

Lewkowitsch has found their solidifying point (titer test) to be 11.1°–11.9°, and the iodine absorptions from 83.2 to 85.6 per cent.

#### EXAMINATION OF COMMERCIAL SPERM OIL

The peculiar physical characters and chemical constitution of sperm oil afford ample means for its detection and determination in presence of other oils. This is important, as the high price of sperm oil renders it liable to be mixed with or replaced by other oils.

Adulterants of sperm oil, with the exception of bottlenose oil, may be detected by a careful application of the following tests:—

The specific gravity of sperm oil averages .878, and never exceeds .884. If lower than the latter figure the possible adulterants of the sample are *hydrocarbons* and *shark oil*, the latter itself largely adulterated with hydrocarbon oil.

The viscosity of the sample should be compared with that of a genuine specimen (see "Viscosity"). The observation should be made at three temperatures at least, 15° C., 50° C., and 100° C. being suitable. Any admixture will be shown by the more rapid change in the viscosity of the sample by increase of temperature. At the ordinary temperature, sperm oil has a lower viscosity than any other non-drying fixed oil.

The determination of the saponification-equivalent of the sample furnishes a valuable means of detecting fatty oils. As 100 parts of

sperm oil neutralise only from 12.3 to 14.7 parts of potassium hydroxide, while nearly all other oils require from 17.0 to 19.7 parts, the proportion of foreign fatty oil in sperm may be approximately ascertained by the equation—

$$F = (P - 13.2) \times 18.5,$$

in which P is the percentage of potassium hydroxide required to saponify the sample, and F is the percentage of foreign oil.

The nature and determination of the saponification-products afford the most satisfactory means of detecting adulterations of sperm oil, which, when genuine, yields from 60 to 63 per cent of insoluble fatty acids, and 39 to 41.5 per cent of ether-residue consisting of higher alcohols. No other animal or vegetable oil except shark-liver oil, and oils from allied *Cetacea* (e.g., bottlenose oil), is known to yield more than 2 per cent. to ether, and, with few exceptions (e.g., porpoise oil and some varieties of whale oil), all other fixed oils yield fully 95 per cent. of insoluble fatty acids, and from 10 to 12 per cent. of glycerol. Hence, in a case of adulteration of sperm oil with any other fatty oil, estimation of the ether-residue will detect the admixture and determine the proportion. Thus, pure sperm oil yielding an almost constant proportion of 40 per cent. of ether-residue, a mixture consisting of equal parts of sperm and some other oil, will give but 20 per cent. of residue. In other words, the percentage of real sperm oil in the sample may be ascertained with considerable accuracy by multiplying the percentage of ether-residue by 2.5. Some specimens of shark-liver oil yield a considerable proportion of ether-residue, and hence if shark oil be present the ether process will be rendered inaccurate. Genuine shark-liver oil has a comparatively high specific gravity, .911 to .929, and has a very high halogen-absorption, besides giving a well-marked violet coloration and great increase of temperature with strong sulphuric acid.

The foregoing process, if used without discretion, would fail in the case of a mixture of mineral oil and a fatty oil in certain proportions, but a careful consideration of the results and further examination of the products will allow of such a mixture being readily distinguished from sperm oil. Thus from an inspection of the figures in the following table it appears that while the saponification-products yielded by sperm oil would be approximately simulated by those given by a judicious mixture of mineral oil with rape oil, in the latter case the sum of the fatty acids and ether-residue would be several units less than 100, and there would be a notable proportion of glycerol produced.

Besides, the ether-residue would be insoluble in cold rectified spirit, and to obtain a mixture of the same specific gravity as sperm oil, so very light a mineral oil would require to be used that it would necessarily be liquid, even at 0° C., and would have so low a flashing point that it could without difficulty be detected in, and even distilled out of, the original oil or the ether-residue. Sperm oil does not flash below 260° C

	PRODUCTS OF THE SAPONIFICATION OF 100 PARTS OF OIL			
	Fatty Acids	Glycerol	Ether-residue	
			Percentage	Characters
Sperm oil	60 to 64	none	3.9 to 4.15	Solid, soluble in spirit.
Ordinary fixed oil	95 to 96	10 to 11	5 to 15	Liquid, insoluble in spirit
Mineral oil	none	none	100	
Rape oil, 60, Mineral oil, 40, }	57.6	6	40	Liquid, insoluble in spirit

The color-reaction with sulphuric acid (page 85) is often a useful test for the purity of sperm oil. The genuine oil gives a brown coloration, becoming somewhat darker with a tinge of violet on stirring. Shark-liver oil gives a well marked violet color when tested in the same manner, the tint changing to red or reddish-brown on stirring.

#### DEGLING OIL BOTTLENOSE OIL

(See also page 101.) Several species of toothed cetaceans yield an oil analogous to that obtained from the cachelot or sperm whale. The chief of these in economic importance is the product from the degling or bottlenose whale (*Hyperoodon rostratus*),<sup>1</sup> which is known in commerce as "Arctic sperm oil."

Bottlenose oil deposits more or less spermaceti when cooled, but the yield is not nearly as large as that obtained from the head-matter and oil of the sperm whale, though of good quality and high melting point. Bottlenose oil often has a more or less unpleasant odor, but this peculiarity, together with the small proportion of free acid present in the crude oil, can be removed to a great extent by agitation with a solution of sodium carbonate, or by analogous treatment. The refined oil is straw yellow.

<sup>1</sup> There has been much confusion respecting the bottlenose, at least eight different whales and dolphins having been designated by that name.

The chemical constitution of dogling oil was first pointed out by Scharling (*Jour. f. Pract. Chem.*, 1848), who found it to consist essentially of the ester of a higher monatomic alcohol, dodecatyl doglate,  $C_{17}H_{35}.C_{10}H_{21}O_2$ , and hence to yield on saponification dodecatyl alcohol and doglic acid. Further investigation on this point is desirable.

*Dodecatyl alcohol*,  $C_{12}H_{25}OH$ , has been described under sperm oil. The crude product obtained from bottlenose oil by the writer, by agitating the aqueous solution of the saponified oil with ether and separating and evaporating the ethereal solution, has similar characters to the product obtained in a similar manner from sperm oil. The colorless alcohol, or mixture of homologous alcohols, obtained by distilling the ether residue *in vacuo*, was found by the author to melt at  $19^{\circ}C$ , and to have an ultimate composition agreeing closely with the formula  $C_{12}H_{26}O$ . The undistilled portion had a higher melting point.

*Doglic acid*,  $C_{13}H_{27}O_2$ , is the next higher homologue of oleic acid, which body it closely resembles. It is liquid at ordinary temperatures, and is converted into solid doglaidic acid by treatment with nitrous acid. Specimens of fatty acids prepared by the author from several specimens of bottlenose oil have been found to have a specific gravity of 896, their combining weights ranging from 275 to 294. An acid with 19 carbon atoms would have a molecular weight of 296, while that of oleic acid is 282.

Bottlenose oil presents the closest resemblance to sperm oil. In its specific gravity (876 to 881), viscosity, solubility in acetic acid, saponification-equivalent, and behavior with strong sulphuric acid and the elaudin-test, it presents no tangible difference from sperm oil. On saponification it yields from 61 to 65 per cent of fatty acids, and from 37 to 41 per cent. of ether-residue, in this respect simulating true sperm oil in the closest manner. Lewkowitsch gives figures for the mixed fatty acids as follows: Solidifying point (titer test),  $83^{\circ}$ – $86^{\circ}$ ; melting point,  $10.3^{\circ}$ – $10.8^{\circ}$ ; and iodine absorption, 82.2–83.3 per cent. The only differences observed by the author in the course of a series of very careful comparative examinations of sperm and dogling oils have been the slight tendency of the latter to gum or thicken on exposure, and the somewhat higher melting point of the fatty acids from sperm oil. In commerce the two oils are distinguished by their taste.

### Spermaceti.

*French*—Cétine, blanc de baleine *German*—Wallrath

(See also table on p 102 ). Spermaceti exists in solution in the oil from the sperm whale, bottlenose whale, dolphin, and allied cetaceans, but not in the oil from the whalebone whales. It is present most abundantly in the oil from the head cavities, and is commonly stated to be a special product thereof. This is an error, the oil from the blubber also depositing spermaceti on cooling, and in practice the head and blubber oils are treated together.

Crude spermaceti forms crystalline scales of a yellowish or brownish color. It is purified by fusion, pressure, and boiling with a solution of potash, to remove adhering oil and neutralise traces of acid. In practice, the complete removal of the oil is not aimed at, as a small proportion is found to confer desirable properties on the product. It is then re-melted and cast into cakes.

As thus obtained, spermaceti is a snow-white or transparent body of marked crystalline structure. It fuses at  $43^{\circ}$  to  $49^{\circ}$  C.<sup>1</sup> The specific gravity at the ordinary temperature is commonly between .942 and .946, but varying statements are made, probably owing to difficulty attending the determination, in consequence of crystalline structure of the substance. Much more reliable determinations can be made of the specific gravity in the molten condition, which ranges between .808 and .812 at a temperature of  $98^{\circ}$  to  $99^{\circ}$  C.

Spermaceti is insoluble in water, but dissolves in boiling alcohol, ether, chloroform, carbon disulphide, and fixed and volatile oils. Cold alcohol dissolves the adhering oil only. From its solution in hot alcohol or ether it separates in crystalline form, and, after repeated purification in this manner, the melting point reaches to  $53.5^{\circ}$  C., and the crystals consist of pure cetin.

CETIN or CETYL PALMITATE,  $C_{18}H_{37}O \cdot C_{16}H_{33}O$ , is the chief constituent of spermaceti, which, in addition, contains certain homologous ethers. Thus, on saponification it yields —

<i>Acids</i>		<i>Alcohols</i>
Lauric, . . .	$C_{12}H_{25}O_2$	Lethal, or dodecetyl alcohol, $C_{12}H_{25}O$
Myristic, . . .	$C_{14}H_{29}O_2$	Methal, or tetradecyl alcohol, $C_{14}H_{29}O$
Palmitic, . . .	$C_{16}H_{33}O_2$	Ethal, or cetyl alcohol, $C_{16}H_{33}O$
Stearic, . . .	$C_{18}H_{37}O_2$	Stethal, or octadecyl alcohol, $C_{18}H_{37}O$

. 1 The figure commonly stated as the melting point of spermaceti really refers to the solidifying point as determined by the titer test. The spermaceti from bottlenose oil melts at a sensibly higher temperature than that from true sperm oil.

CETYL ALCOHOL,  $C_{16}H_{33}OH$ , may be obtained in a state of approximate purity by saponifying spermaceti previously crystallised from hot alcohol. On evaporation of its ethereal solution, cetyl alcohol remains as a white or yellowish white, tasteless, odorless, crystalline mass, melting at  $49.5^{\circ}C$ . When carefully heated it distils without decomposition at about  $400^{\circ}C$ , and is volatile with the vapor of water. It is quite insoluble in water, but readily soluble in alcohol, ether, and petroleum spirit.

When heated with potash-lime to a temperature of  $250^{\circ}$  to  $280^{\circ}C$ , cetyl alcohol is converted into potassium palmitate, with evolution of hydrogen.

Cetyl alcohol heated with glacial acetic acid forms cetyl acetate,  $C_{16}H_{33}C_2H_3O_2$ , a crystalline body melting at  $22^{\circ}$  to  $23^{\circ}$ , and boiling at  $200^{\circ}$  under a pressure of 15 millimetres.

The proportion of potassium hydroxide required for the saponification of spermaceti is about 12.8 per cent, corresponding to a saponification-equivalent of 438. The molecular weight of cetyl palmitate is 480, and hence these figures point to the presence of a notable proportion of lower homologues of palmitic acid, such as have been proved by other means to exist in spermaceti.

On saponification, agitation of the aqueous solution of the resultant soap with ether, and subsequent decomposition of the soap solution with an acid, the author found a sample of spermaceti to yield—

Higher alcohols, melting at $47.5^{\circ}C$ ,	51.48 per cent
Fatty acids, mean combining weight, 231.4,	52.96 „

Pure cetyl palmitate would yield, theoretically.—

Cetyl alcohol, melting at $49.5^{\circ}C$ ,	50.41 per cent
Palmitic acid, combining weight, 256,	53.33 „

#### COMMERCIAL SPERMACETI

Spermaceti is liable to turn yellow and rancid on exposure to air. Hehner found two out of three samples to be wholly devoid of free acid, while the third had an acidity corresponding to 0.81 per cent. of free palmitic acid. The behavior on saponification, together with its physical characters, amply suffice to identify spermaceti and to detect any admixture.

Spermaceti is somewhat liable to adulteration,—stearic and palmitic acids, stearin, tallow, and paraffin wax being possible additions.

According to the German Pharmacopœia, 1 part of spermaceti should be completely dissolved by 40 parts of boiling rectified spirit

(absence of *fats*); after cooling the solution and filtering from the crystalline mass, the filtrate should not have an acid reaction, and should yield at most but a slight precipitate on addition of water (absence of *fatty acids*). On repeating the boiling after the addition of 1 part of dry sodium carbonate, the cold filtrate, on being acidulated, should merely become turbid.

*Palmitic* and *stearic acid* will be detected and determined by estimating the free acid of the sample, by titration with standard alkali and phenolphthalein, any proportion of acid less than 1 per cent being neglected. An admixture of beeswax would somewhat increase the acidity of the sample. Added fatty acids may also be detected by melting the sample in a test-tube immersed in boiling water, agitating with two measures of ammonia of 960 specific gravity, and allowing the whole to cool. If the spermaceti be pure, it will rise to the surface and leave the ammonia nearly or entirely clear, but if adulterated with stearic acid, a thick white emulsion will be formed, which retains the spermaceti if the proportion of the adulterant be large, but allows it to rise and form a separate layer if the stearic acid is present only in moderate amount. One per cent of the adulterant is said to be recognisable by this test.

*Tallow* and *stearin* are recognisable in spermaceti by the test already given, by the change in the fracture, feel, and appearance of the sample; and by the tallowy smell produced on heating. They will also be indicated by the results of the saponification of the sample. In presence of either adulterant the percentage of alkali required for saponification will be increased, the saponification-equivalent correspondingly lowered, while the ether-extract will be diminished and the percentage of fatty acids increased almost in direct proportion to the extent of the adulteration. The saponification equivalent of spermaceti averaging about 438 and that of tallow about 288, each unit per cent. of the adulterant will reduce the saponification equivalent by 1.5. Thus, if a sample be found to require 1478 per cent. of KHO for saponification, corresponding to an equivalent of 380, the percentage of tallow may be assumed to be

$$\frac{(438 - 380) \times 2}{3} = 38.7 \text{ per cent}$$

If free fatty acids be present, together with neutral fats, the same method of calculation will show approximately the sum of the two adulterants and, the fatty acids having been previously determined, the proportion of fats can be ascertained; or, preferably, the fatty

acids may be previously determined in the same portion of the sample, and only the additional quantity of alkali required for the saponification of the neutral fat taken into account in the calculation. The ether-residue from genuine spermaceti being 50 per cent., and from fatty acids and neutral fats practically *nil*, the percentage of such adulterants can be ascertained with accuracy. Each unit per cent. of ether-residue obtained represents 2 per cent. of real spermaceti in the sample.

*Paraffin* diminishes notably the specific gravity of the sample, yields 100 per cent. of ether-residue, neutralises no alkali, and cannot, by admixture with any proportion of fatty acid or fat, be made to give results on saponification similar to those yielded by genuine spermaceti. Thus, a mixture of equal parts of paraffin and tallow will yield 50 per cent. of ether-residue, but the saponification-equivalent will be about 576. If desired, any paraffin which may be present can be isolated and determined by treating the sample with concentrated sulphuric acid in the manner described under "Beeswax." Allowance being made for such admixture, the proportion of any other adulterant simultaneously present can be ascertained in the manner already described. Pure spermaceti does not absorb iodine. Lewkowitsch has found in commercial samples absorptions of 3.52 to 4.09, due probably to small amounts of sperm oil.

### Beeswax.

*French*—Cire d'abeilles    *German*—Bienenwachs

(See also table on page 102.) Beeswax is the material of which the honeycomb of bees is composed. To obtain the wax the honey is drained off, the comb expressed, melted in water, the impurities allowed to subside, and the wax allowed to cool or run into suitable moulds.

**YELLOW WAX.**—Thus obtained, beeswax is a tough, compact, solid substance, of a yellowish or brownish color, with a slight lustre and a finely granular fracture. Its taste is faint and slightly balsamic, and the odor is honey-like and characteristic. It does not feel greasy to the touch.

**WHITE OR BLEACHED WAX.**—By exposure to moisture, air, and light, beeswax becomes decolorised. It may also be bleached by cautious treatment with chromic or nitric acid, but chlorine cannot be advantageously employed owing to the formation of chlorinated substitution-products which give rise to hydrochloric acid when the



**WAX** is burnt. It may also be bleached by boiling it with a dilute solution of potassium dichromate and sulphuric acid. The wax thus treated has a greenish color from the presence of chromium compounds, which it holds very persistently, but which may be removed by boiling the product one or more times with a solution of oxalic acid. It is not every kind of wax which can be effectually bleached. The presence of a small proportion of fatty matter appears to facilitate the process. Bleached wax has its chemical composition somewhat altered by the treatment to which it has been subjected.

Beeswax can be volatilised almost without change in a vacuum. When distilled under the ordinary pressure, it yields a variety of products, among which acrolein does not appear to occur. It is insoluble in water, but dissolves readily in fixed oils, carbon disulphide, and in about 10 parts of boiling ether or turpentine. According to Hager, ether dissolves only about half the wax at the ordinary temperature, and benzene and petroleum spirit about 27 per cent. It is nearly insoluble in cold alcohol, but dissolves in about 300 parts of the boiling liquid, leaving only a small yellowish brown residue. On cooling, the solution deposits a whitish crystalline substance, while the filtrate is yellowish, and is not rendered turbid by addition of water. The portion soluble in cold alcohol consists of aromatic and coloring matters, together with a small quantity of fatty matter to which the name of cerolein has been given. The portion of beeswax dissolved by a moderate quantity of hot alcohol consists chiefly of cerotic acid and its homologues, whilst the undissolved part is myricin.

Schwalb has separated from beeswax two hydrocarbons—heptacosane,  $C_{27}H_{56}$ , and hentriacontane,  $C_{31}H_{64}$ —having melting points of  $60.5^\circ$  and  $67^\circ$  respectively. According to Schwalb, small quantities of myricyl and other alcohols also occur.

F. Nafzger has shown that the free acids of beeswax consist chiefly of cerotic acid, melting at  $78.5^\circ$ , mixed with a small quantity of acids of the oleic series. By fractional precipitation of the alcoholic solution with magnesium acetate a small quantity of an acid was obtained which melted at  $89^\circ$ , and had a composition either identical with that of melissic acid,  $C_{26}H_{52}O_2$ , or with the next homologue,  $C_{28}H_{56}O_2$ .

**CEROTIC ACID**,  $C_{26}H_{52}COOH$ , crystallises from fusion in small grains. It exists in beeswax in the free state, in a proportion usually between 12 and 16 per cent. It dissolves in hot alcohol, but is almost wholly deposited on cooling. It is soluble in hot ether, but is said to be insoluble in chloroform. Lead cerotate is insoluble in alcohol or ether.

To prepare cerotic acid, beeswax should first be repeatedly treated with boiling alcohol. The deposit which separates from the alcohol on cooling is melted, and treated with hot alcohol and potash in faint excess in the manner described for the determination of cerotic acid (page 215). The liquid is then diluted with an equal measure of water, and the unsaponified matter extracted by repeatedly agitating the liquid with hot petroleum spirit. The solution of the soap is then separated and decomposed by dilute acid, the separated cerotic acid being washed, fused, and purified by recrystallisation from boiling alcohol.

The proportion of cerotic acid in beeswax, or rather the proportion of total free acids calculated as cerotic, can be determined as described on next page. The unsaponified portion of the wax consists of myricin, which can be purified by agitation with boiling alcohol and fusion.

MYRICIN is the chief constituent of beeswax insoluble in alcohol. It is a solid, wax-like body, melting at  $64^{\circ}\text{C}$ . On saponification, it yields a palmitate, myricyl alcohol, and a small quantity of soap from an acid of the oleic series. Hence myricin has essentially the constitution of myricyl palmitate.

MYRICYL ALCOHOL,  $\text{C}_{26}\text{H}_{54}\text{O}$ , may be prepared by heating myricin or beeswax itself in a closed vessel for an hour or two with excess of alcoholic potash, nearly neutralising the excess of alkali with acetic acid (using phenolphthalein as an indicator), and precipitating the turbid liquid with excess of lead acetate. The precipitate, consisting of a mixture of lead soaps and myricyl alcohol, is washed, dried, and exhausted with hot ether or petroleum spirit in a Soxhlet's tube. On evaporating the solvent, the wax-alcohol is obtained in white glittering crystals, which may be purified by washing with cold alcohol and recrystallisation from ether. It may also be prepared in a similar manner from carnauba wax.

Myricyl alcohol is a crystalline silky substance, melts at  $85^{\circ}$  to  $86^{\circ}$  to a colorless liquid, and solidifies to a fibrous mass at about  $1^{\circ}$  lower. It is insoluble in water, scarcely soluble in cold alcohol, ether, or benzene, and but little in cold chloroform. It dissolves readily in boiling alcohol, ether, chloroform, benzene, and petroleum spirit. When fused with potassium hydroxide, or heated to  $220^{\circ}\text{C}$  with potash-lime as long as hydrogen is evolved, it is converted into potassium melissate,  $\text{KC}_{26}\text{H}_{53}\text{O}_2$ , which, on solution in water and treatment with an acid, gives melissic acid.

MELISSIC ACID,  $\text{HC}_{26}\text{H}_{53}\text{O}_2$ , crystallises in lustrous white plates or

needles, melts at  $89.9^{\circ}$  to  $90.2^{\circ}$ , and solidifies at  $89.2^{\circ}$ . It is readily soluble in hot alcohol, chloroform, petroleum spirit, and carbon disulphide, but only sparingly in boiling ether. Lead mellissate melts at  $118^{\circ}$  to  $119^{\circ}$ , solidifies at  $117.5^{\circ}$ , is sparingly soluble in boiling toluene and glacial acetic acid, and insoluble in alcohol and ether.

#### ANALYSIS OF GENUINE BEESWAX

The proportion of *cerotic acid* in beeswax can be ascertained by titration with standard acid and phenolphthalein in the usual way, but, owing to the very high combining weight of the acid, the operation must be conducted with extreme care. O. Hehner recommends that alcoholic potash should be used, and that it should be prepared from pure potash and from spirit which has been redistilled from caustic alkali. It should be about one-third normal—that is, 1 c.c. should correspond to 3 to 4 c.c. of normal acid. The alkali should be standardised several times with the acid, and the results should not vary by more than 0.5 c.c. of standard alkali for each 10 c.c. of acid used. 5 grm. of the wax should be heated in a flask with 50 c.c. of methylated spirit which has been redistilled from caustic soda. When the wax is perfectly melted, an alcoholic solution of phenolphthalein is added in not too small an amount. The indicator must not be acid, as is frequently the case, but must previously have been rendered pink by addition of alkali in faint excess. The standard solution of alcoholic potash is then added drop by drop, the liquid being kept well agitated until the pink color becomes permanent, when the volume of alkali employed is observed. The combining weight of cerotic acid being 410, a volume of standard alkali corresponding to 1 c.c. of normal acid represents 0.410 grm. of cerotic acid. The percentage of cerotic acid may be found by multiplying the percentage of KHO required for neutralisation by 7.31. As the volume of standard alkali required by 5 grm. of wax amounts to only a few cubic centimetres, a very finely graduated burette should be employed.

Hehner found by this process, in sixteen samples of English unbleached wax, proportions of free acid, calculated as cerotic acid, ranging from 12.15 to 15.71 per cent, the average being 14.4. Seventeen samples of foreign wax gave very similar results, but showed a somewhat wider variation, the extreme numbers obtained being 12.17 per cent from a dark-brown Mauritian wax, which showed signs of having been burnt in the process of manufacture, and 16.55 per cent. from a dark-brown wax from Gambia. In wax bleached by air and light the proportion of free acid is practically unchanged, but in wax

bleached by chromic acid mixture it may be increased to 17 or 18 per cent. Hehner's results have been confirmed by Hubl, who found in twenty samples of yellow wax proportions of free acid varying from 13.9 to 15.3, the average being 14.6 per cent.

It is evident that the foregoing rapid and simple volumetric process fails to prove the actual nature of the free acid; but by operating on a somewhat larger quantity of beeswax the same method serves as the first step towards the actual isolation of cerotic acid, the quantity obtained being sufficient for the determination of the fusing point and other data. The unsaponified portion consists principally of *myricin*, which can be separated and weighed as such, or its nature and composition may be deduced from the results of its saponification in the following manner:—

The experiment by which the proportion of cerotic acid in beeswax was ascertained by titration with alcoholic potash and phenolphthalein may be extended in such a way as to obtain a determination of the *myricin*. For this purpose a further exactly known volume of standard alcoholic potash should be run into the flask, the quantity used being equivalent to about 25 c. c. of normal acid. A reflux condenser is then attached to the flask, and the liquid briskly boiled for one hour, when the solution should be clear, or nearly so. The flask should be agitated at intervals to remove any particles of wax which may have adhered to the sides of the flask above the liquid. The condenser is then detached and the solution titrated back from a very delicate burette with seminormal acid. The alkalinity which has disappeared, expressed in terms of normal acid, represents the *myricin* which has been saponified. One c. c. of normal acid, or 0.0561 gram of KHO neutralised, corresponds to 0.676 g.m. of *myricin*. Hubl found twenty samples of yellow wax to require from 7.3 to 7.6 per cent of KHO for the saponification of the *myricin*, which figures correspond to proportions of that body varying from 88 to 91.6 per cent. These results fully confirm those of Hehner, who found in sixteen samples of yellow English wax proportions varying from 85.95 to 89.05, the average being 88.1.

When determined volumetrically by the above method, the cerotic acid and *myricin* together usually amount to somewhat more than 100 per cent., the average being, according to Hehner, 102.5. It is evident, therefore, that wax requires more alkali for saponification than would be required for a mixture of pure cerotic acid and *myricin*.

The results above recorded prove that genuine beeswax is of approximately constant composition. Hehner's experiments show that

the proportion the cerotic acid bears to the myricin in English beeswax (unbleached) averages 1 6 12, while Hubl finds ratios varying from 1 5 94 to 1 6 24

*Saponification in the Cold*—Henriques determines the saponification value in the cold as follows. The acid value is determined by dissolving 8 grm of the wax in 25 c.c. of petroleum spirit with the aid of heat and titrating with half-normal alcoholic sodium hydroxide, using phenolphthalein as indicator. If necessary, the liquid is warmed again, 25 c.c. of normal alcoholic hydroxide added, and allowed to stand in the cold for twenty-four hours, when complete saponification will take place. The saponification value is determined by titrating the excess of alkali.

J. Werder (*Chem. Zeit*, 1898, 38 and 59) finds that the Zeiss butyro-refractometer may advantageously be employed in the examination of different kinds of wax, especially when the amount of material at disposal is very limited, and that the indications obtained with it are quite as valuable as in the case of oils and fats. Owing to the high melting point of the wax, it is necessary to work at a higher temperature than usual, preferably 66° to 72° C, and then to reduce the results to the normal temperature, 40° C. As shown in the annexed table, the figures given by genuine beeswax vary from 42 6° to 45 4°, the great majority of specimens falling between 44° and 45°, and it seems to make little or no difference to the refractive power whether they are tested before or after bleaching. Samples 19 to 24 had previously been examined chemically, and had been rejected on the ground of their abnormal acid and ester numbers, which were as follows —

NUMBER OF SAMPLE	ACID NUMBER <sup>1</sup>	ESTER NUMBER <sup>1</sup>
19	18 48	60 64
20	127 1	13 4
21	59 08	3 36
22	104 7	14 3
23	41 0	57 0
24	106 0	48 1

No. 24 is a product called "Glanzwachs," obtained by adding some of the mixture of stearic and palmitic acids as used in the manufacture of stearin candles (No. 28) to a genuine wax, this being a form of adulteration commonly employed in Switzerland

<sup>1</sup> The acid number is the number of milligrams of potassium hydroxide required for the neutralisation of the free acid, and the ester number the number of milligrams required to saponify the esters in one gram of the sample. The figures are expressed as per cent in the table on page 222

## REFRACTIVE POWER OF DIFFERENT KINDS OF WAX

	SAMPLE	TEMPERATURE OF REFRACTION AT	
		OBSERVATION	100° C
1	Bleached, from Egypt	66.0	44.1
2	" " Turkey	67.0	44.8
3	" " Moldavia	66.5	44.2
4	Yellow, " Egypt	66.0	42.8
5	" " Monte Christo	71.0	44.8
6	" " France	67.5	44.1
7	" " Sway	67.0	42.6
8	" " California	69.5	45.2
9	" " North Africa	71.0	45.0
10	" " Masowah	71.5	44.3
11	" " Italy	70.0	44.9
12	" " " } different samples	70.0	44.0
13	" " " }	68.5	44.6
14	" " Mexico	69.5	44.2
15	" " " } different samples	67.0	45.3
16	" " Syria	69.5	44.2
17	" " Candiana	68.0	45.4
18	" " Smyrna	70.0	44.7
19	Bleached, in chips (professedly genuine)	70.5	41.3
20	White Church candles	67.5	32.0
21	" " "	68.0	32.5
22	" " "	68.5	32.6
23	Yellow wax, source unknown	66.0	38.4
24	Wax adulterated with No. 28	65.5	38.8
25	Paraffin	65.0	22.5
26	Ceresin	77.0	41.0
27	Tallow	71.5	43.5
28	Stearin candle material	70.0	30.0
29	Carnaubia wax	91.0	66.0
30	Japan wax	71.0	47.0

## ADULTERATIONS OF BEESWAX

Commercial beeswax is liable to a number of adulterations, among which the following are recorded:—Water; mineral matters, as kaolin, gypsum, barium sulphate, and yellow ochre, sulphur, starch and flour, resinous bodies, as colophony, galipot, and burgundy pitch; fatty bodies, as stearic acid, stearin, Japan wax, and tallow, paraffin and ozokerite, and vegetable waxes, as carnauba wax. Spermaceti is also said to have been used.

Water has been met with in beeswax to the extent of 6 per cent., being purposely introduced. It may be detected and estimated as described under "Lard."

Mineral matters may be detected and determined by igniting the wax. They will also remain insoluble on dissolving the sample in turpentine, chloroform, or benzene. As much as 17 per cent. of yellow ochre has been found in unbleached beeswax.

Starch and flour will be left undissolved on treating the wax with warm turpentine. The liquid may be filtered, the residue washed with

a little ether, and examined under the microscope with solution of iodine. 60 per cent of starch has been met with. Small quantities of starch or flour may exist in genuine wax that has been rolled or pressed, the rollers or press being dusted over with flour to prevent the wax from sticking.

*Sulphur* has been found as an adulterant of unbleached wax. It may be detected by boiling the sample with a weak solution of soda, and adding lead acetate to the cooled liquid, when a black or brown precipitate will be produced if sulphur be present.

According to Weinwurm (*Analyst*, 1897, 242), 2 or 3 per cent of cerasin or paraffin, or 5 per cent of rosin, may be detected as follows: 5 gm of filtered wax are saponified in 25 c.c. of seminormal alkali and the alcohol removed. 20 c.c. of glycerol are run in, the whole warmed in the water-bath till solution is effected, and 100 c.c. of boiling water added. Pure wax gives a clear, transparent, or translucent solution, through which ordinary printed matter may be read with ease. Five per cent of cerasin or rosin yields a cloudy liquid, and the print is no longer legible; 8 per cent of cerasin causes a decided precipitate. If the solution is clear, 3 per cent, or, if it is opaque, 2 per cent. of cerasin is added to another sample of the wax, and the saponification repeated, when from the appearance of the soap solution the presence or absence of either impurity may be deduced.

R Henriques (*Analyst*, 1897, 292) reports favorably on the above process, but simplifies it by applying the Leffmann-Beam alkali-glycerol method for saponifying. A piece of wax about the size of a pea is boiled in a test-tube for three or four minutes with 5 c.c. of alkali glycerol (25 c.c. sodium hydroxide solution, sp. gr. 1.383, and 125 c.c. pure glycerol). The solution, which is at first quite clear, becomes gradually cloudy. After boiling for about the time mentioned, the oil collects in a layer and the underlying fluid becomes clear. The bubbles of the boiling mass also now become smaller and the glycerol commences to distil. As soon as this point is reached the heating is discontinued. The fluid is now poured into another test-tube, in order to separate it from the unsaponified portion, an equal weight of hot water is added, and the liquid boiled and allowed to cool. In the case of pure wax the solution will be either quite clear and transparent, or at any rate sufficiently translucent to allow of large printed matter being read through it, as described by Weinwurm. Should, however, on the contrary, as much as 5 per cent. of foreign hydrocarbons be present, the fluid will be quite opaque. With an admixture of only 3 per cent. of cerasin or paraffin, the indication

is uncertain, and the further treatment recommended by Weiswurm to meet such cases should be followed.

Japan wax and other *fatty substances* (e.g., tallow, stearin, stearic acid) may also be detected by boiling 1 gm. of the sample with 1½ gm. of borax and 20 cc. of water, when the aqueous liquid will become milky or gelatinous on cooling. With pure beeswax it remains clear or becomes but slightly turbid, and carnauba wax and rosin behave similarly.

The specific gravity of beeswax is a useful indication of the presence of foreign admixtures. Great discrepancies occur in the recorded specific gravities of possible adulterants of beeswax, as determined by various observers, the differences being probably due to the faulty methods of observation. The subject has been investigated by W. Chat-taway in the author's laboratory, with the following results.—

1. Hager's method is objectionable, owing to the anomalous contraction caused by sudden cooling of the fused substance

2. If sudden cooling be avoided, the determination may be made by immersing the fragment in dilute alcohol or ammonium hydroxide, adjusting the specific gravity of the liquid until identical with that of the wax, and then ascertaining its specific gravity by one of the usual methods. To prepare the fragments, a good plan is to melt the wax in a clock-glass or flat-bottomed capsule placed over a beaker of boiling water, and then remove the source of heat and allow the water in the beaker to cool spontaneously. Small blocks can then be cut from the solidified wax with a knife, or cylinders removed with a corkborer. Another good plan is to suck up the molten wax into a piece of quill-tubing, the upper end of which is then closed by the finger, while the lower is immersed in cold water. This causes the wax to set at the orifice of the tube, and so closes it. The tube is then supported in a vertical position, and the contents allowed to solidify spontaneously. Owing to the mode of cooling, the wax forms a smooth cylindrical stick, readily removable from the tube, the central portion is always free from cavities and air-bubbles. The cubes or cylinders are then painted over with a wet brush to prevent the adherence of air-bubbles, and then cautiously lowered (not dropped) into the spirit by means of a pair of forceps or a glass rod bent into the form of a hook.

3. In the case of a crystalline substance, such as spermaceti or Chinese wax, the determination of the specific gravity of the solid substance is very unsatisfactory, but the difficulty is wholly avoided if the determination be made on the molten wax at the temperature of boiling water.



The melting and solidifying point of a sample of wax will often afford valuable information, but unfortunately the figures recorded as the melting points of various waxes exhibit great discrepancies, owing to the different methods employed.

The following table shows a number of results obtained in the author's laboratory by the examination of specimens of waxes and analogous bodies. The specific gravities were determined by the methods just indicated, the melting points by method *a*, page 34, and the solidifying points by method *d*, page 37.—

SUBSTANCE	SPECIFIC GRAVITY, WATER AT 15.5° C = 1		TEMPERATURE OF CHANGE OF PHYSICAL STATE, °C	
	At 15-16° C	At 98-99° C	Melting Point	Solidifying Point
Beeswax, yellow	963	822	63.0	60.5, no rise
" chemically bleached	964	827	63.5	62.0, no rise
" air-bleached	961	818	63.0	61.5, no rise
Spermaceti, bottlenose	912	808	49.0	48.0, no rise
Carnauba wax		812	85.0	81.0, no rise
Chinese wax ..		810	81.5	80.5, no rise
Japan wax ..	984-993	875-877	51-53	41.0, rising to 48
Myrtle wax ..		875	40.5	39.0, no rise
Tallow, pressed		861	44.5	32.5, rising to 34
Suet, beef ..	944	860	49.0	32.5, rising to 34.5
Stearic acid		810	56.5	54.5, no rise
Colophony ..	1.071		-	-
Paraffin wax ..	909	757	54.5	54.0, no rise
Ozokerite, refined		753	61.5	60.0, no rise

The following table gives the specific gravities and melting points of waxes and some other bodies, as determined by other observers —

SUBSTANCE	SPECIFIC GRAVITY AT 15-16° C		TEMPERATURE OF CHANGE OF PHYSICAL STATL., °C		
			F Rudorff		Various
	Dietrich	Various	Melting Point	Solidifying Point	Melting Point
Beeswax, yellow	973	959-969	62 0-62 5	62 0-62 5	{ 63-64 67-70 11-49 83-85 42-53 36-49
" bleached	963-964				
Spermaceti . .	960	942-946	44 0-44 5	44 0-44 5	
Carnauba wax..		995-1 000			
Japan wax . .	975	984-1 000	52 5-54 5	41 0, rising to 46	58-65
Tallow . . . .	952-961	925-940	42 5-50 5	33 0-39 5, rising 4-5°	
Stearic acid . .	971-972	964-986			
Colophony . . .	1 045-1 108	1 070-1 090	.		
Paraffin wax .	913-914	868-915	.		48-72
Cerasin . . . .	918-927				

A further insight into the nature and proportion of the adulterants which the foregoing tests may have indicated to be present in a sample of beeswax, can be obtained by a careful determination of the percentages of alkali required for the neutralisation of the free acid and for the complete saponification of the sample. For the method of operating see page 216. The following table, drawn up from the results of Hehner, Hubl, and the author, shows the behavior with potassium hydroxide of such probable adulterants of beeswax as are soluble in oil of turpentine:—

SUBSTANCE	AVERAGE PERCENTAGE OF KHO REQUIRED			RATIO OF A B
	A For Neutralisation of Free Acid	B For Saponification of Esters	A + B Total.	
Unbleached beeswax	2.0	7.5	9.5	1.375
Chemically bleached beeswax	2.4	7.1	9.5	1.296
Spermaceti	traces	12.8	12.8	
Carnauba wax	4-8	7.6	8.0-8.4	1 { 19.0 9.5
Chinese wax	traces	6.3	6.3	
Japan wax	2.0	19.5	21.5	1.975
Myrtle wax	0.3	20.5	21.8	1.683
Tallow and stearin	1.0	18.5	19.5	1.185
Stearic acid (commercial)	20.0	none	20.0	
Coleophony	18.0	1.0	19.0	18.1
Paraffin wax	none	none	none	
Cerium and ozokerite				

*Spermaceti* is not usually an adulterant of beeswax, but there have been occasions when its substitution would have been profitable and may have been practised. It is the only adulterant which would cause the sample to show less free acid, and yet require an increased proportion of alkali for its saponification, at the same time yielding less glycerol and reducing the specific gravity and melting point. In the absence of carnauba wax, a direct indication of the presence and proportion of spermaceti may be obtained from a determination of the melting point of the higher alcohols of the sample.

From an inspection of the table it appears that *carnauba wax* requires for complete saponification a proportion of alkali not very different from that required by beeswax, but is distinguished from the latter by the smaller (but very variable) proportion of alkali required by the free acid. An admixture of carnauba wax will be further indicated by the increased specific gravity and higher melting point of the sample.

Another proof of the presence of carnauba wax is obtainable by removing free acid by alcohol and alcoholic potash, saponifying the separated neutral wax, precipitating the solution with lead acetate, and exhausting the precipitate with petroleum spirit, and decomposing the lead soap with hot hydrochloric acid. Beeswax, when thus treated, yields a product which is chiefly palmitic acid (melting point,  $62^{\circ}\text{C}$ ), while the product similarly obtained from carnauba wax is largely cerotic acid (melting point,  $79^{\circ}\text{C}$ ).

If the proportion of alkali required for total saponification exceed 9.5, or, at the outside, 10.0 per cent. of the wax, the presence of some adulterant is certain. Japan wax, myrtle wax, tallow, and stearin all require proportions of potash not far from 20 per cent. Hence each 0.1 per cent. of KHO required in excess of the normal proportion 9.5, indicates the presence of about 95 per cent of one of these adulterants.

*Japan* and *myrtle wax* are denser than beeswax, and *tallow* and *stearin* somewhat lighter, but they all agree in having a notably lower fusing point than pure beeswax, and yield glycerol on saponification. In doubtful cases, a determination of the glycerol by the permanganate process may be resorted to, when the amount found multiplied by 10 gives the approximate weight of the adulterant. The presence of fatty substances is also indicated by the qualitative tests with borax (page 220).

*Free stearic acid* is readily distinguished from the neutral fats by the large proportion of alkali required in the first stage of the process, in fact, the percentage of this adulterant may be calculated by multiplying by 5 any excess of potash required for saponification above the normal proportion of 2 per cent. Stearic acid is also indicated by the sodium carbonate test. It is employed less frequently than other adulterants of beeswax, as it notably diminishes the malleability of the substance.

*Colophony* or *rosin* requires somewhat less alkali for its neutralisation than is taken by stearic acid, and the proportion is not very constant. Its presence is further indicated by the increased specific gravity of the sample. It may be detected with certainty, even if present to the extent only of 1 per cent., by boiling 5 grm. of the sample for one minute with 20 c.c. of nitric acid of 1.33 specific gravity. When cold, the liquid is diluted with an equal volume of water and agitated with excess of ammonia. With pure wax a yellow solution is produced, but if resin be present nitro-compounds are formed, which impart to the liquid a blood-red or reddish-brown tint, varying in intensity with

the proportion of the adulterant. Cases have been recorded of factitious beeswax composed of 60 per cent. of paraffin and 40 of yellow resin, covered with a thin layer of genuine beeswax. On boiling the sample with 15 times its weight of alcohol of 870 specific gravity, the paraffin was left in fused colorless globules having a specific gravity of 910, while the solution yielded the resin on evaporation. Such a residue would give a marked resinous odor when heated, but if the proportion of the sample soluble in alcohol be small, such a test must not be regarded as absolute proof of the presence of added resin, as many specimens of genuine beeswax behave similarly.

*Paraffin, cerasin, and ozokerite* are the only adulterants of beeswax which tend to reduce in a notable degree the proportion of potash required for saponification. They also reduce the specific gravity in a marked manner, but this indication has little more than a qualitative value. In a sample consisting solely of beeswax and hydrocarbon wax the proportion of the former may be deduced with considerable accuracy from the results of the saponification, each 0.1 per cent of KHO required representing 1.053 per cent of beeswax in the sample.

*Determination of Fatty Alcohols and of Paraffin and Cerasin*.—An adulteration of beeswax with less than 6 per cent of cerasin or paraffin cannot be detected with certainty by any of the ordinary methods, because the relations between the free fatty acid and saponifiable and unsaponifiable matters in genuine beeswax vary within somewhat wide limits. The detection of smaller quantities of these adulterants can only be made possible by a direct determination of the hydrocarbons present, and C. Mangold (*J. S. C. I.*, 1891, 860) describes a modification of a method recently brought out by A. and P. Buisine with that object. The method is based on the observation of Dumas and Stas, that if a saponified wax be heated with potash-lime, the fatty alcohols are decomposed with formation of fatty acids and evolution of hydrogen, the volume of which becomes a measure of the fatty alcohols present, whilst the hydrocarbons may be dissolved out of the residue and weighed. The improvements of the method consist in the simplification of the apparatus and a more exact knowledge of the conditions to be observed. From 2 to 10 gm. of the wax are saponified by melting with potash-lime. The solid dry soap is then powdered and well mixed with three times its weight of potash-lime, and placed in a strong pear-shaped flask, in which it is heated to 250° for two hours. The apparatus for conducting this operation is shown in the sketch. *A* is an iron vessel with a lid fastened down by screws and filled with mercury. The flask *E* is connected, gas-tight, with a Hofmann's

burette, *H*, for measuring the hydrogen evolved. *T* is a thermometer and *V* a temperature regulator. *K* is a condensing tube for mercury vapor. It is advisable that the heating at 250° be continued for three hours to secure completion of the reaction, after which the flask is allowed to cool, and is broken up to liberate the residual mass, which is then powdered and extracted with petroleum spirit in a Soxhlet apparatus. The residue left on evaporation of the petroleum spirit is dried at 110° and weighed. Genuine beeswax examined by this method gives always some hydrocarbons, but the experience of Mangold and other observers is to the effect that the quantity is almost invariably between 12.5 and 15.6 per cent. The mean of these quantities, or 13.5, must, therefore, be deducted from the total hydrocarbon found, and the difference is the amount of hydrocarbon added by way of adulteration.

On account of the difficulty of saponifying certain waxes with alcoholic lye, Benedikt and Mangold (*J. S. C. I.*, 1891, 860) recommend the following modification of Hehner's method —

1. The acid number is ascertained as usual, 7 to 10 grm. being employed for the test.

2. Instead of the saponification number the "total acid number" is determined, by which is understood the quantity of potassium hydroxide necessary for neutralising a mixture of fatty acids and monatomic alcohols obtained after previously decomposing the saponified wax by dilute hydrochloric acid. To obtain this mixture, 20 grm of potassium hydroxide are dissolved in 15 c.c. of water and boiled; to this, during continuous stirring, are added 20 grm of the wax, which has been melted on the water-bath. The mixture is heated and stirred for ten minutes more, then diluted with 200 c.c. of water, heated again, and acidified with 40 c.c. of hydrochloric acid slightly diluted with water. It is boiled until the upper part appears clear, allowed to stand, and the wax-cake boiled, first with water containing some

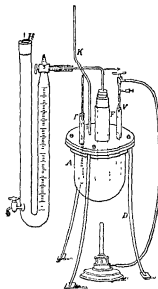


FIG. 9.

hydrochloric acid, and subsequently twice with water alone. The wax cake is dried with filter paper, melted in the drying oven, and the liquid filtered. The filtrate solidifies as it cools. 6 to 8 grm of the substance thus obtained are treated with alcohol free from acids, heated on the water-bath, and titrated after phenolphthalein has been added. The total acid number thus obtained is somewhat lower than Hubl's saponification number. If  $s$  be the acid number,  $S$  the total acid number, and  $a$  the other number, we have Hubl's saponification number,  $a + s$ , and—

$$a = \frac{56100 (S - s)}{56100 - 18 S} \quad S = \frac{56100 (a + s)}{56100 + 18 a}$$

The total acid numbers of various kinds of yellow beeswax of different origins ranged from 88 to 93, as an average figure, 92.8 is given, corresponding to the saponification number 95. The amount of wax ( $W$ ) contained in cerasin is then determined by the formula.—

$$W = \frac{100 S}{92.8},$$

or, more accurately,

$$W = \frac{97.72 S}{92.75 - 0.00298 S}$$

If, however, small quantities (6 per cent. or less) are mixed with beeswax, this test is no longer applicable, and Buisson's method must be used instead. When stearic acid or resin is present, the acid number is higher; if  $\sigma$  be the average acid number of such additions, these additions are calculated by the formula.—

$$K = \frac{100 (s - 2 \sigma)}{\sigma - 2 \sigma}$$

With stearic acid, as used for technical purposes,  $\sigma = 200$ , hence we have in this case—

$$K = \frac{10 (s - 2 \sigma)}{18}$$

When fats or tallow are present, the following formula has to be used —

$$W = \frac{100 (S_f - S) a}{(S_f - S) a + (S - S_w) b},$$

where  $S$  is the total acid number,  $S_w$  the total acid number of pure beeswax,  $S_f$  that of fat,  $a$  the quantity of wax necessary for obtaining 1 grm of substance, as above described, by the treatment with dilute

hydrochloric acid, and *b* the quantity of fat which yields 1 grm. of insoluble fatty acid.

A ratio number may be calculated, as noted above, from the total acid and the acid value, not from the ether- and acid-value. Thus, Lewkowitsch ("Chem. Anal. of Oils, Fat, and Waxes") notes that a normal wax having the saponification value 95 would furnish a ratio number as follows —

$$S - s = 72.77 - 20 = 52.77$$

The ratio number of pure wax is not so constant as has been assumed. A sample of wax having the acid value 18 and saponification value 90 (corresponding to the total acid value 88), may yet be pure, a large number of yellow waxes from various sources having given numbers between 88 and 93 for *S*.

The determination of the ratio number alone will not suffice, as it is possible to prepare, without wax, mixtures having a normal ratio number. Thus, Lewkowitsch calculates that a mixture of Japan wax 37.5 parts, stearic acid 6.5 parts, and cerasin or paraffin wax 56 parts, will give the normal ratio number of acid value to ether-value of 3.71. It is evident that the examination must be supplemented by other determinations, *e.g.*, iodine value, hydrogen liberated on heating with potassium hydroxide, and estimation of the hydrocarbons.

The following are some results obtained by Buisson in the examination of beeswax and adulterants —

	MELTING POINT, °C	ACIDS SOLUBLE IN WATER	FREE ACIDS	TOTAL ACIDS IN 1 GRM. EXPRESSED AS MILLIGRAMS KOH	IODINE NUMBER	CC. HYDROGEN ON TREATMENT WITH KOH, 0° AND 760 MM.	PERCENT AGE OF HYDRO- CARBON
Japan wax ...	47-54	2	18-28	216-222	6-7.55	69-71	0
China wax .	53.5	2	22	218	6.86	72.3	0
Vegetable waxes	47-64	2	17-19	218-220	6.6-8.2	73-74	0
Carnauba wax	83-84	0	4-6	70-82	7-0	73-76	1.6
Mineral waxes	60-80	0	0	0	0-0.6	0	100
Paraffins .	33-74	0	0	0	1.7-3.1	0	100
Wax from "suint"	62-66	0	95-115	102-110	13-18.5	0	14-18
Waxy acids from "suint"	50-62	0	155-185	159-180	2.6-2.8	0	* 0
Suet ....	42-50.5	0	2.75-5	196-213	27-40	52-60	0
Stearic acid .	55.5	0	204	209	4	0	0
Roasin ....	..	0	108	178	135.6	35	0
Yellow beeswax	62-64	0-1	19-21	91-97	8-11	53-57.5	12.5-14.5
Bleached beeswax	63-64	0-2	20-23	93-110(?)	2-7	53-57	11-13.5

### Carnauba Wax. Carnahuba Wax

(See also pages 102, 221, 222, and 227) This is a very hard, sulphur-yellow, or yellowish-green substance, melting at about  $84^{\circ}$ , of nearly the same specific gravity as water, and leaving, on ignition, a trifling quantity of ash, which often contains iron oxide.

Carnauba wax has a very complex composition. It consists of a mixture of higher fatty acids and alcohols, together with the others of these bodies. Berard found free cerotic acid in the portion of the wax soluble in hot alcohol, while Story-Maskelyne found myricyl alcohol in the same solution. This result is confirmed by H. Sturke (*J. S. C. I.*, 1884, 448). He states the alcoholic solution to contain myricyl alcohol, and a small quantity of myricyl cerotate, which is soluble in boiling alcohol to the extent of 0.82 gm. per litre. The free myricyl alcohol and that obtainable by saponifying the myricyl cerotate together amount to 45 per cent. of the entire wax.

By saponification of carnauba wax, Sturke obtained the following bodies:—a *hydrocarbon*, melting at about  $59^{\circ}$ , *ceryl alcohol*,  $C_{25}H_{52}OH$ , a crystalline body melting at  $76^{\circ}$ . The sum of these did not exceed 2 per cent. of the wax, *myricyl alcohol* (45 per cent.); a *diatomic alcohol*,  $C_{18}H_{36}(CH_2OH)_2$ , melting at  $103.5^{\circ}$ , an *acid* of the formula  $C_{25}H_{48}COOH$ , melting at  $72.5^{\circ}$ , and isomeric with lignoceric acid; *cerotic acid*, the chief acid of carnauba wax, melting at  $79^{\circ}$ , or an acid isomeric therewith, a *hydroxy acid* of the formula  $CH_2OH C_{17}H_{34}COOH$ .

Carnauba wax when in a separate state is readily recognised by its physical characters and the results of its saponification. It is sometimes employed as an adulterant of beeswax, in which its presence may be recognised by the high specific gravity and melting point of the substance, and by the melting point of the fatty acids produced by the saponification of the neutral ethers of the sample. The presence of carnauba wax in soap is best recognised by mixing the sample with sand, drying thoroughly, and exhausting the mixture with petroleum spirit (boiling at about  $100^{\circ}$ ) or hot toluene in a Soxhlet's tube. The residue left on distilling off the solvent is then treated in the manner directed for the preparation of myricyl alcohol from beeswax. The weight of myricyl alcohol divided by 0.45 gives approximately the amount of carnauba wax in the quantity of soap employed.

E. Valenta has found carnauba wax in a number of commercial cerasins and paraffins which were characterised by their high melting points and great hardness. It is employed to impart these properties and to give a peculiar lustre to the wax. Valenta gives the following



figures showing the influence of carnauba wax, melting at 85° C., on the melting point of mixtures containing it.

PERCENTAGE OF CARNAUBA WAX	MELTING POINT (° C) OF SUBSTANCE OR MIXTURE		
	With Stearic Acid	With Cerauin	With Paraffin Wax
0	58.50	72.10	60.15
5	69.75	70.10	73.90
10	73.75	80.50	79.20
15	74.55	81.60	81.10
20	75.20	82.53	81.50
25	75.80	82.95	81.75

These results show a very marked increase in the melting point of the substances by the addition even of 5 per cent of carnauba wax. Further additions increase the melting point in a diminished ratio.

The proportion of carnauba wax existing in admixture with the foregoing bodies, or with Japan wax, can be ascertained by determining the percentage of potash required for the neutralisation of the free acid and for the saponification of the esters of the sample, and by the determination of the unsaponifiable matter.

### Blown Oils, Oxidised Oils, Base Oils.

Various products known by these or similar names are now manufactured by blowing a stream of air through fatty oils. The oils which lend themselves most readily to the treatment are cottonseed, rape, and linseed oils, but the process is also carried out with olive, lard, and other oils. The oil is usually heated by a steam-coil at the commencement of the process to a temperature of 70° C, though this is not strictly necessary, at least with certain oils, and in any case care must be exercised in order to avoid too high a temperature (above 80° C). The process usually lasts from twelve to forty-eight hours, according to the nature of the oil under treatment, the character of the product desired, and the size and power of the apparatus. Great heat is developed and the oil increases in specific gravity and viscosity. The product can be varied by arresting the process at any particular point. Blown oil is usually of a clear yellow color, with a disagreeable smell and taste suggesting its origin. It is very viscous and often as dense or denser than castor oil, from which it differs by not dissolving readily in alcohol and in being soluble in petroleum spirit. Its perfect miscibility with heavy mineral oils gives it an

advantage over castor oil in the manufacture of lubricating mixtures for heavy machinery. Mineral oil and castor oil are mutually soluble only to a very limited extent, but by addition of some other oil, such as tallow oil, perfect union can be effected. When the oxidation of cottonseed oil is pushed to an extreme, the product has a density of 885 and is not readily miscible with heavy mineral oils. Blown oils yield sebacic acid on dry distillation, and contain but an insignificant proportion of unsaponifiable matter. The odor, taste, and color-reaction of the oil with sulphuric acid will afford an indication of its origin, and more definite information can be obtained by an examination of the physical and chemical characters of the fatty acids produced by its saponification.

The process of blowing results in a change in the fatty acids, a notable proportion of which after the process is soluble in water. The insoluble acids have a mean combining weight considerably below the original, and are regarded by Fox and Baynes (*Analyst*, xii 33) as probably "oxyacids of the acrylic series." The glycerin, as determined by the permanganate process, apparently increases somewhat, but this effect is probably due to the formation of soluble products, which, like glycerol, yield oxalic acid by oxidation with permanganate. On saponification blown oils usually yield very dark soaps. The following figures, obtained by the analysis of blown oils, have been published by Fox and Baynes (*loc cit*) —

	LINSEED	COTTONSEED	RAFFINED
Glycerol (apparent)	12.85 per cent	11.68 per cent	11.32 per cent
Free fatty acids	2.73	5.15	3.70
Insoluble fatty acids	87.67 "	85.50 "	84.70 "
Comb. wt. of insol. acid	258.4	176.0	180.0

Fox (*Oil and Col. Jour.*, 1887, 549) has also published the following figures, showing the change produced in oils by blowing air —

	LINSEED		COTTONSEED		RAFFINED	
	Before	After	Before	After	Before	After
Specific gravity	935.4	986	916	968.5	927	985
Glycerol	9.36	12.85	9.84	11.32	9.61	11.68
Free fatty acids	2.10	2.73	2.60	3.70	3.20	5.35
Insol. fatty acids	95.70	87.67	95.43	84.70	95.65	85.50

## HIGHER FATTY ACIDS.

Under the denomination of "fatty acids," used in its widest sense, are included the whole series of homologous acids of which formic acid is the lowest member, together with the various homologous acids of the acrylic or oleic series, the peculiar acids obtained by the saponification of castor and drying oils, and many others.

The lower acids of the formic, acetic, or stearic series have been fully considered in Volume I., page 485 *et seq*.

The following tables give some particulars respecting such higher fatty acids as are of interest or importance as constituents of the fixed oils or fats. Some information as to the analytical characters of caprylic, pelargonic, and capric acids will be found in Volume I. Palmitic, stearic, and oleic acids are so important and of such frequent occurrence that they are described at length in subsequent sections. Further information respecting arachidic, erucic, linolic, and ricinolic acids will be found in the sections treating of the oils of which they are especially characteristic—namely, arachis oil, rape oil, linseed oil, and castor oil.

The methods of detecting or determining the lower homologues of the stearic series are described on pages 50, 58, and 189.

It will be noted that the acids of the stearic series become less fusible as the number of carbon atoms increases.

In a similar manner, the boiling points of the acids of the stearic series rise with an increase in the number of carbon atoms. The higher members cannot be distilled under the ordinary atmospheric pressure without suffering more or less decomposition, but may be distilled unaltered under diminished pressure. The table shows the boiling points of some of the stearic series under diminished pressure.

Similarly, oleic acid may be distilled in a vacuum, or in a current of superheated steam at 250° C, without material alteration, but if distilled with contact of air it is partially decomposed, with formation of carbon dioxide, paraffinoid hydrocarbons, and acetic, caproic, caprylic, capric, sebacic, and other acids.

In the following tables the acids of the different series are arranged together. Their relationship is evident from the following list of the acids containing 18 carbon atoms in the molecule:—

$C_{18}H_{36}O_2$ , Stearic Acid	$C_{18}H_{32}O_2$ , Linolenic Acid, Isohnenic Acid
$C_{18}H_{34}O_2$ , Oleic Acid, Elaidic Acid	$C_{18}H_{34}O_2$ , Ricinolic Acid, Isoricinolic Acid
$C_{18}H_{32}O_2$ , Linolic Acid, Stenolic Acid	Ricinelaiddic Acid, Rape Acid

A.—HIGHER ACIDS OF THE ACETIC OR STEARIC SERIES,  $C_nH_{2n+1}COOH$

NAME	FORMULA	CHIEF SOURCE	MELTING Pt. °C	BOILING POINT, °C	OTHER CHARACTERS
Caprylic,	$C_8H_{17}O_2$	Coconut oil and butter-fat	15.5	At 760 mm 226	Crystallizes in needles or plates. Soluble in 400 parts of boiling water, much deposited on cooling, readily soluble in alcohol, ether, and benzene. Barium salt moderately soluble
Pelargonic, Capric,	$C_{10}H_{19}O_2$ $C_{10}H_{19}O_2$	Butter-fat, cod-liver and coconut oils	31.2	At 100 mm 261.5 At 760 mm 268-270	Crystallizes in plates. Slightly soluble in water, easily in alcohol and ether. Barium salt soluble in boiling water
Undecylic,	$C_{11}H_{21}O_2$	But of <i>Urschellaria Cuthbertii</i>	21-23	At 100 mm 212.5 At 760 mm 278-289	Crystallizes in scales. Faint odor resembling caproic acid
Lauroic,	$C_{12}H_{25}O_2$	Coconut, pyramidal, croton, laurel oils, palm-rum beans, undigerm-acid	43.5	In vacuo 102 At 100 mm 176 Ducis readily with open steam	Solidifies from fusion in scales. Lead salt insoluble in ether, sparingly in alcohol
Tridecic, Myristic,	$C_{13}H_{27}O_2$ $C_{14}H_{29}O_2$	Coconut and dika oils, nutmeg-butter, and spermaceti	53.8	In vacuo 121-122 At 100 mm 248 slightly volatile with open steam	Insoluble in water, lead salt soluble in alcohol, insoluble in ether
Isostearic, Palmitic,	$C_{16}H_{33}O_2$ $C_{16}H_{33}O_2$	Cereus oil	65 63	In vacuo 198-199 At 100 mm 271.5 At 760 mm 330-336, with slight decomposition	See "Palmitic Acid"
Stearic,	$C_{17}H_{35}O_2$ $C_{18}H_{37}O_2$	Oil of seeds of <i>Datura stramonium</i> Must fats	71-71.5	In vacuo 154.5-155.5 At 100 mm 291 At 760 mm 360, with slight decomposition	Soluble in hot alcohol and ether, lead salt sparingly soluble in ether and petroleum spirit.
Nondecic, Arachidic,	$C_{19}H_{39}O_2$ $C_{20}H_{41}O_2$	Synthetic. Arachis oil	77		Sparingly soluble in cold, easily in hot alcohol. Lead salt insoluble in ether
Behenic, Lignoceric,	$C_{22}H_{45}O_2$ $C_{24}H_{49}O_2$	Oil of ben Archeus oil, beechwood tar	80-82 80.5		Lead salt insoluble in alcohol or ether
Carnaubic,	$C_{24}H_{49}O_2$	Carnauba wax and wool wax.	77-79		
Hyenic,	$C_{26}H_{53}O_2$	Secretion of the anal glands of the striped hyena	77.8		
Cerotic,	$C_{26}H_{53}O_2$	Beeswax and carnauba wax	90		
Melissic,	$C_{28}H_{57}O_2$	Beeswax.			

**B.—HIGHER ACIDS OF THE ACRYLIC OR OLEIC SERIES,  $C_nH_{2n-3}O_2$  or  $C_nH_{2n-1}COOH$ .**

NAME.	FORMULA.	CHIEF SOURCES.	MELTING POINT, ° C.	OTHER CHARACTERS.	ISOMERIC (OR POLYMERIC) ACIDS PRODUCED BY THE ACTION OF NITROUS ACIDS ON NATURAL ACIDS
Hypogaeic.		Arachis oil	33	Forms colorless crystals, readily soluble in alcohol and ether. Combines with $H_2$ . Yields gaidic acid with nitrous acid and sebatic acid on distillation. Lead salt soluble in ether.	<i>Gaidic acid</i> forms a crystalline mass melting at 39°. Volatilises almost unchanged. Readily soluble in alcohol. Combines with $H_2$ .
Phytololeic.		Said to exist in sperm oil	30	Differs from hypogaeic acid in not yielding sebatic acid on distillation.	
Aselleic, . . . Oleic.	$C_{17}H_{31}O_2$ $C_{17}H_{31}O_2$	Said to exist in sardine oil The majority of fatty oils form the oleic of commerce.	14	See "Oleic Acid."	<i>Elaidic acid</i> , produced by action of $HNO_3$ on oleic acid. Fearly plates melting at 45°, and distilling almost unchanged.
Isotoleic.		By distillation of hydroxy-stearic acid	45	Soluble in alcohol and ether. Unites with $H_2$ . Behaves like oleic acid, when fused with alkali. Readily less soluble in ether than lead oleate.	
Rapaeic, . . . Dagaeic, . . . Jacoleic, Erudeic or Brassic.	$C_{19}H_{35}O_2$ $C_{19}H_{35}O_2$ $C_{22}H_{39}O_2$	Rape oil (Zellner, <i>J. S. C.I.</i> , 1886, 661). Said to exist in bottlenose oil. Said to exist in cod-liver oil. Rape oil, black and white mustard oils.	78 16 33-34	Resembles oleic acid.  Crystallises from alcohol in long luminous needles, which melt at 78°. It is less soluble in ether than its lead oleate. Yields acetate and arachidate when fused with $KHO$ .	<i>Desferdric acid</i> , produced by action of $HNO_3$ on oleic acid.  <i>Ercosidic or Brassidic acid</i> , produced by action of nitrous acid on erucic acid, melts at 58°. Lead salt nearly insoluble in warm ether.

*E Ricinolic acid* combines with two atoms of bromine or iodine, does not oxidise in the air, is gradually solidified by nitrous acid, and forms a lead salt soluble in ether. With potassium permanganate in alkaline solution it yields a trihydroxystearic acid. No homologues of ricinolic acid are known and the isomers have been little studied.

### Recognition and Determination of Fatty Acids

The methods available for the detection and to some extent for the determination of the higher fatty acids are based on the characters just described. In many cases it is unnecessary to effect actual separation of the fatty acids in a mixture, it being sufficient to ascertain the joint amount, or to determine indirectly and approximately the proportion of the acids of different origin known to be present.

#### METHODS NOT INVOLVING SEPARATION

*a* Free fatty acids can be accurately determined by titration in alcoholic solution with standard caustic alkali, using phenolphthalein to indicate the point of neutrality. The mode of operating is fully described on page 104. Neutral bodies—*eg*, fats and hydrocarbons—do not interfere. Mineral acids and acid salts must first be removed by agitation with water, or determined by titration in alcoholic solution with methyl orange as indicator, and resin acids must be separated or duly allowed for. In the case of a mixture of several fatty acids the result is best expressed in terms of the principal or most characteristic acid present, and in most cases such a mode of statement gives a close approximation to the total of the free fatty acids present.

Conversely, when the substance under examination consists wholly of a mixture of fatty acids, titration with standard alkali suffices to ascertain the mean combining weight of the mixed acids. This is found by dividing the number of milligrams of fatty acids employed for the titration by the number of cubic centimetres of normal alkali required for neutralisation (see page 237).

In cases of a mixture of two homologous acids, the nature of which is known or can be ascertained by other means, the result of the titration gives the means of ascertaining the proportions in which the two constituent acids exist in the mixture. An example of the application of the method to this purpose is given on page 241.

*b* The method of Koettstorfer (page 56) may be regarded as a process of approximately ascertaining the mean combining weight of

the fatty acids of an oil without actually isolating them. If the saponification-equivalent of the oil be multiplied by 0.95, the mean combining weight of the acids will be obtained with tolerable accuracy. The method is, of course, only applicable to oils yielding approximately 95 per cent of fatty acids on saponification. With oils like shark and sperm oil and the true waxes the process is quite useless. With pure esters it is in some respects preferable to a titration of the previously isolated fatty acids, as there is less danger of alteration by oxidation or the loss of soluble fatty acids in the course of preparation.

*c* The titration of a mixture of oleic acid with acids of the stearic series by means of Hubl's reagent (page 64) allows the former constituent to be determined with considerable accuracy. As 282 parts of oleic acid,  $C_{18}H_{34}O_2$ , assimilate 254 parts of iodine,  $I_2$ , the iodine-absorption divided by 0.9 gives the percentage of *oleic acid* present. Linolic acid and its homologues assimilate  $I_2$ , and hence their presence renders the determination of the oleic acid excessive, but the method is still applicable if the mode of calculation be modified accordingly. Oleic and linolic acids have so very nearly the same molecular weight (282-280), that the latter may be regarded as absorbing twice as much iodine as the former, or 180 per cent against 90. Hence, if 90 be subtracted from the observed iodine-absorption of the mixed acids, and the difference be divided by 0.9, the dividend will be the number of parts of linolic acid in 100 parts of the mixture. If acids of the stearic series are also present, they must be separated or duly allowed for in making the calculation, which is vitiated if linolenic acid also be present. If the percentages of stearic, oleic, and linolic acids in a mixture of the three be represented respectively by *s*, *o*, and *l*, and iodine-absorption by *A*, then, the value of *s* being known, the proportion of the liquid acids will be found by the following equations:—

$$o = 200 - 1.11 A, \text{ and } l = 100 - o - s$$

*d* Useful information respecting the fatty acids present can be obtained by determining the melting point or solidifying point of the substance. When the mixture consists merely of two acids of the stearic series, the determination affords a means of approximately ascertaining their relative proportions. The melting points of various mixtures of the acids of the stearic series have been determined by Heintz, and are given in a tabular form on page 242 *et seq.* The melting and solidifying points of the fatty acids from different fixed oils are more or less characteristic of their origin, as also are their specific gravities and mean combining weights.

The following table gives data obtained in the author's laboratory. The fatty acids were prepared as follows —The oil was saponified with alcoholic potash, the alcohol evaporated, and the residual soap dissolved in hot water and decomposed by dilute sulphuric acid. The liquid having been well boiled, the separated fatty acids were filtered through paper. The higher alcohols of the sperin and bottlenose oils were removed by agitating the solution of the soap with ether, the ethereal layer separated, and the ether dissolved in the aqueous liquid got rid of by warming before liberating the fatty acids. In the case of the other oils the trifling proportion of unsaponifiable matter was ignored.

Kind of Oil	CHARACTERS OF SEPARATED INSOLUBLE FATTY ACIDS				
	Specific Gravity		Melting Point, °C	Solidifying Point, °C	Combining Weight
	At 15.5° C	At 58-59° C			
Olive oil . .	solid	·8430	26.8	21.0	270.4
Arachis oil .	solid	·8460	29.5	28.0	281.8
Rape oil . . . . .	solid	·8448	19.5	18.5	321.2
Cottonseed oil (pressed)	solid	·8407	35.0	32.0	287.2
Sesame oil . .	solid	·8233	23.0	18.6	286.5
Linseed oil . .	·8233	8612	24.0	17.5	307.2
Castor oil . .	·8500	8960	.	.	300.6
Palm oil .	solid	8369	50.0	45.5	269.6
Coconut oil .	solid	.	24.0	20.5	.
Japan wax	solid	8482	56.0	53.0	265.3
Myrtle wax	solid	8370	47.5	46.0	243.0
Lard . . . . .	solid	.	44.0	39.0	276.0
Northern whale oil .	9076	·8595	.	..	298.7
Sperm oil . . . . .	8990	.	.	.	289.4
Bottlenose oil .	8905	.	.	.	294.6

The following results have been communicated by other observers:—

SOURCE OF FATTY ACIDS.	COMBINING WEIGHT	OBSERVER
Tallow, lard, or olive oil	270-285	C R Alder Wright
Castor oil . . . . .	290-296	"
Coconut oil .	196-204	"
Palm oil . .	273	A Norman Tate
Palmnut oil .	211	E Valenta.
Cottonseed oil	275	"
Sesame oil	286	"



The following table gives the melting points and solidifying points of the fatty acids as determined by various observers—

SOURCE OF FATTY ACIDS	Melting Point, ° C	Solidifying Point, ° C	
		Various Methods	Titer Test (Lewkowitzsch)
Olive oil . . . . .	24-27	17-26 4	16 9-26 4
Almond oil . . . . .	13-14	6-12 (t)	9 5-11 8
Arachis oil . . . . .	28-33	24-31	28 1-29 2
Rape oil . . . . .	18-22	12-18	11 7-14 6
Cottonseed oil . . . . .	35-44	32-40	32 2-37 6
Sesame oil . . . . .	23-31	18-28	21 2-23 8
Nigerseed oil . . . . .	25-27		
Poppyseed oil . . . . .	20-21	15 5-17	
Linseed oil . . . . .	17-24	13-20	10 0-20 6
Hempseed oil . . . . .	17-19	14-16	15 6-16 6
Walnut oil . . . . .	15-20	16-17	
Castor oil . . . . .	13	2-3	
Palm oil . . . . .	40-50	36-45 5	35 8-45 4
Palmnut oil . . . . .	21-28		20 -25 5
Cacao butter . . . . .	48-52	40-51	48 -48 27
Nutmeg butter . . . . .	42-43	36-40	35 5-35 95
Shea butter . . . . .	40-58	38-54	58 75-53 8
Coconut oil . . . . .	24-27	16-20	21 2-25 2
Japan wax . . . . .	56-57	53-59	58 8-59 4
Myrtle wax . . . . .	47-48	46	
Lard oil . . . . .	42-43		
Lard . . . . .	35-47	32-43	41 45-42
Compounded lard . . . . .	39-43		
Tallow, mutton . . . . .	46-54		40 15-48 3
" beef . . . . .	43-47		37 9-46 25
Margarine . . . . .	42	40	
Butter-fat (insoluble acids) . . . . .	36-46	37-38	
Sperm oil . . . . .	13	11-12	11 1-11 0
Whale oil . . . . .	14-27	23-24	22 0-23 0

The variations in the melting and solidifying points are in great measure due to the different methods of observation adopted.

The figures have, in some instances, considerable practical value. Thus, the high melting point of the fatty acids obtained on saponification distinguishes cottonseed oil from nearly all other liquid fixed oils of vegetable origin, and enables its presence to be inferred in admixture with other oils; the melting point of the acids from cacao butter is remarkably constant, and is sometimes useful as a test of the purity of the fat, while the solidifying point of the acids from palm oil affords a practical indication of the value of the sample to the candle manufacturer. The same remark applies to the fatty acids of tallow, and a table has been constructed by Dalcan (page 172) by which the proportion of oleic and solid fatty acids which a sample of tallow will yield can be deduced from the solidifying point of the mixed acids.

## SEPARATION OF MIXED FATTY ACIDS.

The actual *separation* of mixed fatty acids is often a problem of extreme difficulty, and indeed cannot in all cases be satisfactorily solved in the present condition of chemistry. Methods for effecting the recognition and separation of the lower members of the stearic series will be found in Volume I, page 485 *et seq.* The principles which have been applied to the fatty acids enumerated in the tables on page 232 *et seq.* include the following —

1 The mixed fatty acids are well washed by agitation with hot water, when those containing 10 atoms or fewer of carbon are dissolved. This process is applied to the analysis of the fatty acids from butter (page 190)

2 The mixed fatty acids obtained by treating the soaps with a moderate excess of dilute sulphuric acid are distilled with water, either with or without the aid of a current of open steam (page 51) This method allows a more or less complete separation of the homologues up to lauric acid from the higher members of the stearic series

3. The acids are converted into barium salts, and the precipitate treated with water or alcohol. The barium salts of lower members up to capric acid can be dissolved out by boiling water (page 192).

4. The alcoholic solution of the acids is precipitated by magnesium acetate. By operating fractionally some useful separations may be effected (see below).

5 The acids are converted into lead salts, which are then treated with ether or alcohol. An application of this principle enables oleic acid and its homologues to be separated from the higher acids of the stearic series

6. Fractional distillation, fractional fusion and pressure, and fractional solution in or crystallisation from alcohol or other solvents, are other processes employed for the separation of the fatty acids.

No precise method of *separating* oleic acid and its homologues from linolic acid has hitherto been devised. Possibly one might be based on the conversion of the acids of the oleic series into isomers of higher melting point and modified properties by means of nitrous acid. Methods 1, 2, and 3 have already been sufficiently described, and those under 6 do not require further notice. Methods 4 and 5, however, are described in detail below.

*Separation of the Higher Fatty Acids of the Stearic Series* — The higher homologues of the stearic series can be separated from the lower members by treatment with hot water or distillation with water and open

steam, and from the insoluble and non-volatile acids of other series by treatment of the lead soaps with ether. By proper application of these methods there may be obtained a mixture of solid, non-volatile homologues of stearic acid, which, according to its origin, may contain more or less lauric, myristic, palmitic, stearic, arachidic, and other less frequently occurring acids of the series. The separation of these homologues is extremely difficult, and a quantitative determination of several immediate homologues occurring together in a mixture is especially so. Advantage may be taken of the limited solubility of *arachidic acid* in alcohol to effect its separation, as is done in Renard's process for the detection of earthnut oil (page 134); and indeed the solubility of the homologues in alcohol rapidly increases with a diminution of the number of carbon-atoms in the acid. For the actual separation of the higher homologues of the stearic series from each other, however, the most satisfactory method is that of Heintz (*Journ f Pract. Chem.*, lxxi. 1), based on fractional precipitation of the alcoholic solution of the acids with magnesium acetate. This salt precipitates acids of the stearic series more easily than it does oleic acid and its homologues, and, of the different homologues of the stearic series, those of the highest molecular weights are thrown down first. In practice, 40 grm. of the mixed fatty acids should be dissolved in such a proportion of hot alcohol that nothing will separate on cooling, even at 0°, and the hot liquid treated with a boiling alcoholic solution of 1½ grm of magnesium acetate. The liquid is well agitated and allowed to become cold, when the precipitate is filtered off and the filtrate treated with a fresh quantity of alcoholic magnesium acetate. This second precipitate is similarly separated, and the treatment repeated as long as anything is thrown down. To induce precipitation of the lower homologues, it becomes necessary to render the liquid alkaline with strong ammonium hydroxide before adding magnesium acetate, and to allow the solution to stand in the cold for twenty-four hours before filtering. The first fractions of the precipitate contain magnesium stearate and any higher homologues, the succeeding portions will consist chiefly of magnesium palmitate, and the last will probably contain myristate; but a portion of the myristic acid, the whole or nearly the whole of the lauric acid, and any oleic acid which may be present will remain in solution, and may be precipitated by addition of lead acetate after neutralising the excess of ammonium hydroxide with acetic acid. The precipitate should be filtered off, washed with cold dilute alcohol, and, if oleate be present, treated with ether. The purified lead precipitate and the various magnesium precipitates should be washed with cold alcohol,

pressed, and decomposed by hot dilute hydrochloric acid, the liberated fatty acids being washed free from mineral acid by repeated agitation with hot water, and further treated as described on page 51. The details of the fractional precipitation should be modified to suit particular cases, and in some instances separation into a smaller number of fractions will suffice.

The several fractions of fatty acids thus obtained, after being weighed if desired, should then be titrated with standard alkali in the manner described on page 104. Five grm of each fraction will be a suitable quantity, and this should be treated with about 30 c.c. of warm spirit (neutral) and titrated with a seminormal solution of caustic soda, a few drops of a solution of phenolphthalein being employed as an indicator, and an accurately divided burette being used. The mean combining weight of the acids constituting a fraction is found by dividing the number of milligrams of fatty acids employed by the number of cubic centimetres of normal alkali required for their neutralisation. Thus, if 5 grm weight of a fraction has been found to require 37.80 c.c. of seminormal alkali for its neutralisation, the mean combining weight of the acids will be 264.5, for:—

$$\frac{5000 \times 2}{37.8} = 264.5$$

As a rule, if the mixed fatty acids be divided into a sufficient number of fractions by precipitation with magnesium acetate, each fraction will contain only two homologues, in which case the result of the titration not only indicates the nature of the homologues present, but in many cases allows of their relative proportion being calculated. Thus, if, in the course of a systematic fractional precipitation as magnesium salts, a fraction of fatty acids be obtained having a mean combining weight of 264.5, it will almost certainly consist essentially of a mixture of stearic and palmitic acids, the former of which has the molecular weight 284 and the latter 256, the difference being 28. Hence, every 1 per cent of stearic acid in the mixture will raise the combining weight .28, or for every unit above 256 found for the combining weight of the fraction 3.57 of stearic acid should be calculated. As with all indirect methods of the kind, the results obtained are fairly satisfactory when both constituents are present in considerable proportions, but are of little value for mixtures in which one constituent very largely predominates.

The titration having been completed, the alcohol may be boiled off and the fatty acids again liberated and subjected to renewed fractional precipitation or crystallisation from alcohol. The products so obtained

can be again titrated, and thus the progress of the isolation and purification of the fatty acids checked in a simple and satisfactory manner.

Valuable information respecting the composition of the various fractions obtained by the precipitation as magnesium salts is obtainable by determining the melting points of the fatty acids. For this purpose they should be purified by single crystallisation from hot alcohol, and dried by pressure between blotting paper. Unfortunately, the melting point of a mixture of two or more homologous fatty acids is not the mean of the melting points of the constituent acids. The melting points of various mixtures of solid fatty acids have been very carefully determined by Heintz, who has also noticed that the mixtures, on solidifying, crystallize in more or less characteristic forms, or remain amorphous, according to the proportions in which the constituents are present. The following are some of the more important of the results of Heintz —

MIXTURES OF LAURIC ACID WITH ITS HIGHER HOMOLOGUES

LAURIC ACID PER CENT	WITH MYRISTIC ACID		WITH PALMITIC ACID	WITH STEARIC ACID
	Melting Point	Solidifying Point	Melting Point	Melting Point
100	43.6	.	43.6	43.6
90	41.3	36.0	41.3	41.5
80	38.5	33.0	37.1	38.5
70	35.1	32.3	38.3	43.4
60	36.7	33.5	40.1	50.8
50	37.4	35.7	47.0	55.8
40	43.0	39.0	51.2	59.0
30	46.7	39.0	54.5	62.0
20	49.6	44.5	57.4	64.7
10	51.8	47.3	49.8	67.0
0	53.8		62.0	69.2

MIXTURES OF MYRISTIC ACID WITH ITS HIGHER HOMOLOGUES.

MYRISTIC ACID PER CENT	WITH PALMITIC ACID		WITH STEARIC ACID
	Melting Point.	Solidifying Point	Melting Point
100	53.8		57.8
90	51.8	45.3	51.7
80	49.5	41.3	47.8
70	46.2	43.7	48.2
60	47.0	43.7	50.4
50	47.8	45.3	54.5
40	51.5	49.5	59.8
30	54.9	51.3	62.8
20	58.0	53.5	65.0
10	60.1	53.7	67.1
0	62.0		69.2

## MIXTURES OF PALMITIC ACID WITH STEARIC ACID

PALMITIC ACID PER CENT	STEARIC ACID PER CENT	MELTING POINT	SOLIDIFYING POINT	MANNER OF SOLIDIFICATION
100	0	62.0		Crystalline scales
90	10	60.1	54.5	Fine crystalline needles
80	20	57.5	53.8	Very indistinct needles
70	30	55.1	54.0	Amorphous, wavy, dull
60	40	56.3	54.5	Large crystalline laminae
50	50	56.6	55.0	Large crystalline laminae
40	60	60.3	56.5	Amorphous, lumpy
30	70	62.9	59.3	Delicate crystalline needles
20	80	65.3	60.1	Delicate crystalline needles
10	90	67.2	62.5	Crystalline scales
0	100	69.2		Crystalline scales

Heintz also noticed that the addition of a third acid, even of higher melting point, to a mixture of two homologous acids causes a lowering of the melting point. This is shown in the following table —

PARTS OF PALMITIC ACID ADDED TO MYRISTIC ACID, 11, MYRISTIC ACID, 6 PARTS	MELTING POINT	MANNER OF SOLIDIFICATION	PARTS OF STEARIC ACID ADDED TO MYRISTIC ACID, 11, PALMITIC ACID, 6 PARTS	MELTING POINT	MANNER OF SOLIDIFICATION
0	35.1	Amorphous, frod-like	0	46.2	Indistinct lamellæ
1	33.9	Amorphous	1	45.2	Amorphous
2	33.1	"	2	44.5	"
3	32.2	"	3	44.0	"
4	32.7	"	4	43.8	"
5	33.7	"	5	44.0	"
6	34.6	"	6	45.6	"
7	35.3	"	7	46.0	"
8	36.0	"	8	46.5	"
9	37.3	Indistinct minute needles			
10	38.8	Minute needles.			

The determination of the melting point of a mixture of two or more fatty acids taken alone is evidently incapable of giving very definite information; but if the observation be associated with other data very useful inferences can be drawn. Thus the following mixtures of homologous fatty acids melt at nearly the same temperature, but may be distinguished by determining their combining weights, by titrating

them in alcoholic solution with standard caustic alkali and phenolphthalein (page 242)

NATURE OF MIXED FATTY ACIDS				MELTING POINT	COMBINING WEIGHT
Lauric	Myristic	Palmitic	Stearic		
30	70	..	..	46.7	210.0
50		50	..	47.0	228.0
	70	30		46.2	239.4
.	50	21	29	46.5	250.0

A method of examining fatty acids, proposed by Benedikt and Ulzer, consists in preparing the acetyl derivatives and then ascertaining the amount of alkali required for saponification; 50 grm. of the fatty acid are boiled with 40 grm. of acetic anhydride, under an inverted condenser, for two hours. The product is boiled with about 500 cc of water, washed till free from acid, dried, and filtered. A known weight is then dissolved in alcohol and directly titrated with standard alkali. Another quantity is then saponified with a known quantity of  $\text{KHO}$ , as in Koettstorfer's process, and the excess of alkali determined by titration with standard acid and phenolphthalein. Benedikt and Ulzer (*Monatshefte*, Jan., 1887) give the following figures obtained by the process —

SOURCE OF FATTY ACIDS	ORIGINAL ACIDS		ACETYLATED ACIDS	
	$\text{KHO}$ p c for Neutralisation	Mean Combining Weight	Without Saponifying $\text{KHO}$ p c	With Saponification $\text{KHO}$ p c
Nut oil.	20.48	273.9	19.80	20.56
Cottonseed oil ..	19.98	280.8	19.57	21.23
Croton oil ..	20.10	279.1	19.57	20.42
Hempseed oil ..	19.94	281.3	19.68	20.43
Almond oil ..	20.16	278.3	19.63	20.23
Olive oil ..	19.71	284.6	19.73	20.20
Castor oil	17.74	316.2	14.28	29.62

The process of Benedikt and Ulzer is based on the assumption that only hydroxylated fatty acids (e.g., ricinolic acid) form acetylated derivatives when heated with acetic anhydride, the others remaining unaltered, so that in the latter case the proportions of alkali required will be approximately the same before and after acetylation. Lewkowitsch (*J. S. C. I.*, ix 842) has published results which appear to prove conclusively that the reaction with acetic anhydride is not so simple or

the figures so reliable as was supposed. Acetic anhydride appears to act on stearic acid to form stearic anhydride and acetic acid. After washing with water the stearic anhydride is but slowly hydrolysed by aqueous potash, but if dissolved in alcohol and titrated with caustic alkali, it undergoes immediate hydrolysis, and hence neutralises the alkali, just like stearic acid. This fact prevented Benedikt and Ulzer from discovering the change. The other higher fatty acids behave similarly. Lewkowitsch points out that, in the light of his researches, the presence of hydroxylated fatty acids (*e.g.*, ricinolic acid) cannot be safely inferred unless the difference in the amount of alkali required for neutralising the fatty acids before and after treatment with acetic anhydride exceeds the limits of possible experimental error. He suggests that while the presence of hydroxylated acids is proved, the best method of estimating the amount will be to saponify the acetylated acids with alcoholic potash, boil off the alcohol, acidulate with sulphuric acid, distil off the acetic acid, and ascertain its amount by titration of the distillate.

*Separation of Acids of the Stearic Series from Fatty Acids of other Series*—The higher homologues of the stearic series of fatty acids being solid at ordinary temperatures, while the fatty acids of other series (*e.g.*, oleic, linolic, myristic) are liquid, a more or less complete separation can be effected by subjecting the mixture to filtration or pressure. The latter plan is employed with considerable success on a large scale. Crystallisation from hot alcohol also serves to free the solid fatty acids from those fluid at ordinary temperatures, but neither plan allows of the latter being obtained even moderately free from admixed solid acids, and such methods are quite useless for quantitative work.

A general method by which stearic acid and its homologues may be separated from oleic and other liquid fatty acids, is based on the fact that the lead salts of the acids of the stearic series are almost insoluble in ether, while the corresponding compounds of the other fatty acids are soluble. Since the lead salts of the solid acids are not wholly insoluble in ether, and those of the drying fatty acids are not completely dissolved, the results are not strictly accurate. The best method of operating is probably that of Muter and De Koningh. Three grm of the fat should be treated, in a flask furnished with a long tube, with 50 c.c. of alcohol and a fragment of potassium hydroxide. The contents of the flask are heated to boiling till saponification is complete, when a drop of phenolphthalein solution is added and acetic acid until the solution is slightly acid. An alcoholic solution of potassium hydroxide is then added drop by drop until a faint permanent pink tint



is obtained, when the liquid is slowly poured, with constant stirring, into a beaker containing a boiling solution of 3 gm. of neutral lead acetate in 200 c.c. of water. The solution is rapidly cooled and stirred at the same time, to induce agglomeration of the precipitate, and the clear liquid is poured off. The precipitate is well washed, by decantation, with boiling water and transferred to a stoppered bottle, in which it is treated with 120 c.c. of ether and allowed to remain twelve hours (Wallenstein and Finck use a Drechsel gas-washing flask having the tube shortened about two-thirds, to contain the ethereal solution, and pass a current of hydrogen through it for about a minute. In the case of white fats the liquid is said to remain practically colorless at the end of twelve hours, but if free access of air is permitted, a dark-yellow solution is produced by oxidation). Lead oleate, hypogaeate, linolate or ricinolate will be dissolved by the ether, leaving lead laurate, myristate, palmitate, stearate, and arachidate undissolved. Lead erucate is sparingly soluble in cold ether, but readily in hot. The contents of the bottle are filtered through a covered filter into a Muter separating-tube (Fig 10), 40 c.c. of dilute hydrochloric acid (1.4) added and the tube shaken till the clearing of the ethereal solution shows that the decomposition of the lead soaps is complete. The aqueous liquid, containing lead chloride and excess of hydrochloric acid, is run off through the bottom tap, water added, and agitated with the ether and the process of washing by agitation repeated until the removal of the acid is complete. Water is then added to the zero mark and sufficient ether to bring the ether to a definite volume (*eg*, 200 c.c.). An aliquot portion of this (*eg*, 50 c.c.) is then removed through the side tap and the residual fatty acid weighed after evaporation of the ether in a current of coal-gas or carbon dioxide. Another aliquot portion of the ethereal solution should be distilled to a small bulk (avoiding complete evaporation of the ether), alcohol added and the solution titrated with decinormal potassium hydroxide and phenolphthalein, from which the fatty acids may be calculated from the result, or their mean combining weight deduced therefrom. A third aliquot part of the ethereal solution should be evaporated at about 60° C in a flask traversed by a rapid stream of dry carbon dioxide.

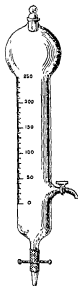


FIG 10.

When every trace of ether is removed, 50 c.c. of Hübl's iodine solution should be added, the stopper inserted and the liquid kept in absolute darkness for twelve hours, after which an excess of potassium iodide solution is added and 250 c.c. of water, and the excess of iodine ascertained with thiosulphate solution in the usual way. From the result the iodine value of the liquid fatty acids is calculated, and an opinion may be formed respecting the proportions of oleic, linolic, and other unsaturated acids present.

The following table shows the results obtained with various fats and oils:—

	IODINE NUMBER OF		OBSERVER
	Sol.	Liquid Fatty Acids	
Lard, American	66.0	101.0 (highest)	v. Raumer.
" Berlin	65.4	101.5	Wallenstein and Finck
" German	92.7	96.6	" "
" Vienna	66.9	96.2 (highest)	v. Raumer
" Hungarian	66.4	95.2	Wallenstein and Finck.
" Roumainian	59.5	96.2	" "
" "		96.0	" "
" "		93.0 (highest)	Muter and DeKoninck
" "		94.0 (highest)	v. A. both
Beef tallow		90.0	Muter and DeKoninck
" " Australian	38.3	92.2	Wallenstein and Finck
" " Berlin	45.2	92.4	" "
" " Hungarian	38.6	92.7	" "
Cottonseed oil		155.0	Muter and DeKoninck
" " "		136.0	v. A. both
" " American, white	104.0	147.5	Wallenstein and Finck
" " " yellow	107.8	147.5	" "
" " Egyptian	106.5	148.8	" "
" " Peruvian	106.8	147.8	" "
Maize oil	122.0	140.7	" "
Nigerseed oil	133.5	147.5	" "
Arachis oil	98.0	125.5	" "
Rape oil	101.1	120.5	" "
Cocnut oil	8.0	54.0	" "

If it be desired to estimate *stearic acid* and its homologues, the lead soaps insoluble in ether should be detached from the filter and heated for some time with dilute hydrochloric acid, the liberated fatty acids being allowed to solidify, and then removed and weighed. The product may contain *arachidic*, *stearic*, *palmitic*, *myristic*, and *lauric acids*, besides the less commonly occurring acids of the same series. A modification of the method specially suited for the determination of *arachidic acid* is described on page 134. If it be found impossible to remove the whole of the fatty acids from the filter, the latter should

be treated with hot dilute hydrochloric acid, and then washed with a mixture of alcohol and ether, the fatty acids being recovered by evaporating the solution so obtained.

Rose (*J S C I*, 1897, 306) recommends the following process. In preparing the fatty acids from the fat, great care must be taken to avoid oxidation. The fat is saponified with an alcoholic solution of potassium hydroxide, decomposed with sulphuric acid, cooled, and the fatty acids transferred to a graduated tube and shaken with an equal volume of ether. When clear, the amount of fatty acid is determined in a portion of the ethereal solution on evaporation, the residue being dried in a current of dry carbon oxide before weighing. A definite volume of the ethereal solution corresponding to about 1 gm. of the fatty acids is then transferred to a 100 c.c. flask, with an excess of lead oxide, diluted to about 80 c.c. with ether, and then allowed to stand in a cool place until the solution becomes strongly alkaline, which will require two to four days, with occasional shaking. The liquid is made up with ether to exactly 100 c.c. Fifty c.c. are passed through a small filter into a tared flask, the filter being kept full as long as possible, and then evaporated to dryness out of contact with the air. After weighing, the lead in the residue is determined as lead sulphate. Trial experiments with oleic acid gave very satisfactory results.

Twitchell (*J S C I*, 1895, 516) recommends the use of petroleum spirit volatile at 80° C, in which lead stearate and palmitate are much less soluble than in ether, but considers Rose's method applicable only when the original fat is perfectly fresh.

Halphen and Bishop (*Analyst*, 1894, 282) recommend Sear's method of separation, as follows.—Ten gm. of the fatty acids are dissolved in 200 c.c. of carbon disulphide in a 200 c.c. flask. To the solution 5 gm. of zinc oxide are added, the flask well corked, and shaken at intervals for six hours. The soluble zinc salts are separated from the insoluble by filtration. The filter is well washed with carbon disulphide, the washings being added to the soluble salts in the tared flask. The carbon disulphide is distilled off, and the residue dried for an hour at 80°, while a current of dry air is passed over them. The increase in weight shows the quantity of zinc salts furnished by the liquid part of the fatty acids. To estimate the combined zinc, 50 c.c. of normal sulphuric acid are added, with constant shaking, until all the acids are liberated. The liquid in the flask, excluding the layer of fatty acid, is made up to 200 c.c. Rather more than 100 c.c. are removed with a pipette and filtered. 100 c.c. of the clear filtrate are then titrated with normal sodium hydroxide, from the result of which the weight of zinc combined with 100 gm. of the fatty acid can be calculated. This is also an index of the molecular equivalent of the acids. The iodine number is determined directly on the acids.

The zinc salts soluble in carbon disulphide, left on the filter, are decomposed

by boiling with hydrochloric acid and their iodine number taken. The soluble zinc salts obtained from pure lard, beef suet, and mutton suet are of an amber color, while those derived from cottonseed oil acids or from lard adulterated with cottonseed oil are orange red.

Iodine numbers for the liquid fatty acids from various sources were found as follows: American lard, 91.95, French lard, 85.61; beef tallow, 75.60, mutton tallow, 80.26, cottonseed oil, 129.03.

Hehner and Mitchell have devised the following method for the determination of *stearic acid*—Prepare a supply of alcohol saturated at 0° C. with pure stearic acid or with stearic acid which only contains traces of palmitic acid. Dissolve from 0.5 to 1 gram of the mixture

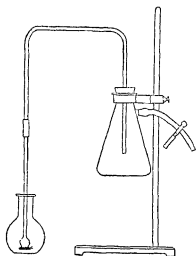


FIG. 11

of fatty acids to be examined, if these are solid, or about 5 gram if fluid, in about 100 c.c. (exact measurement is not necessary) of the stearic alcohol solution. Leave this liquid in an ice-bath over night, agitate the mixture next morning and allow to stand in ice for a short time; filter off while the mixture remains in ice, wash with stearic alcohol solution at 0° C., dry and weigh. Determine the melting point of the product which should not be much less than 68.5° C. Since the sides of the interior of the flask, as well as the residue of crystallised stearic

acid retain a small amount of the alcoholic solution, a correction experimentally found to be 0.005 gram has to be applied, this amount being deducted from the total weight found. In their experiments the authors used methylated alcohol of specific gravity 8183, but obviously the exact strength is a matter of no consequence.

For maintaining a constant temperature, Hehner and Mitchell used an ice-chest consisting of a metal box with sockets soldered to its sides to receive clamps for holding flasks, submerged to the neck in ice-water, in which the determinations were carried out. The metal box was fitted in a wooden box, and the space between the metal and wood

was packed with wool and sawdust, while a cushion of wool and flannel was placed between the lids of the metal and wooden boxes.

For the preparation of the stearic solution about 3 grm. of pure stearic acid were dissolved in about a liter of warm alcohol of specific gravity .8183, and the stoppered bottle containing the solution placed over night in the ice-water (which contained lumps of ice) in the chest, so that the bottle was submerged up to the neck. After twelve hours a considerable portion of the stearic acid had crystallised out. The saturated mother-liquor was syphoned off without removing the bottle from the ice-water. The filtering syphon consisted of a small thistle funnel twice bent at right angles, fitting with its straight limb into a flask in connection with a suction pump. The bulb of the funnel, which was submerged in the ice-cold solution, was covered over with a piece of fine calico. On applying suction, a perfectly clear stearic solution was obtained, saturated at 0° C, or, rather at 0.2° C, which was the temperature almost constantly shown by a standard thermometer.

A precisely similar mode of filtration was also adopted in the quantitative experiments on mixed fatty acids, the thistle funnel used being a miniature one, with a bulb not larger than about  $\frac{1}{4}$  of an inch in diameter. (See Fig. 11 on opposite page.)

#### DETERMINATION OF STEARIC ACID IN MISCELLANEOUS FATS.

	TAKEN GRAM	IODINE NUMBER	STEARIC ACID 0.005 GRM	PERCENTAGE IN FATTY ACIDS
Beef stearin.....	0.3024	20	0.1516	50.19
" " " " " "	0.4174		0.2131	51.05
Oleomargarin ....	1.0107	46.50	0.2295	22
" " " " " "	0.5102	"	0.1104	21.26
" " " " " "	1.1100	"	0.2630	23.6
Margarin I .....	1.0035		0.2405	24.8
" II. ....	0.5000	41.10	0.0586	11.72
Horse-kidney fat ..	0.701	55.4	no deposit	
Cotton oil "stearin" ..	0.9945		0.0334	3.3
Stillings tallow .....		22.87	no deposit	
Oleoco butter .. ....	1.0168		0.3878	40.6
" " " " " "	0.9548		no deposit	
Maise oil .....	5.4184	122	no deposit	
Almond oil .....	5.0240	95.68	no deposit	
Olive oil .....	6.6558		no deposit	
Barthnut oil .. ....	1.0648		0.0751	7.0
			(M P 67° C)	

Numerous determinations of the stearic acid in butter were made. In many cases none, or a minute quantity only, was found. In some

cases phenomena of supersaturation apparently occurred. On the first examination in the morning the solution was perfectly clear, but after shaking the contents and allowing to stand some time longer in the ice, a small but increasing quantity of crystals formed.

The method appears to be inapplicable to the fatty acids from Japan wax. From mixtures of these with pure stearic acid, the latter could only be recovered partially, and in some cases not at all.

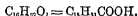
Other methods of separating oleic from stearic acid, or of determining the former in mixtures of the two are described on page 262. A method for separating oleic from palmitic acid is also described on page 262.

*Separation of Fatty Acids from Resin Acids.*—As already pointed out, Twitchell's method has been found to be the most satisfactory (see page 107).

*Separation of Fatty Acids from Soaps, Hydrocarbon Oils, &c.*—The determination of the constituents of complex mixtures of fatty acids with neutral oils, hydrocarbons, &c., has already been described (see table on page 117). Small quantities of neutral fats contained in free fatty acids may be detected by dissolving the substance in hot alcohol and adding a few drops of strong ammonium hydroxide to the solution, in the presence of mere traces of neutral fat, the solution is rendered turbid.

### Palmitic Acid.

*French*—Acide palmitique *German*—Palmitinsäure.



The glyceride of palmitic acid occurs largely in palm oil, Chinese tallow, the fat of coffee-beans, coconut oil, butter-fat, tallow, and lard. Palmitic esters of monatomic radicals exist in spermaceti, beeswax, and opium wax.

Palmitic acid is conveniently prepared from palm oil, which should be saponified with potassium hydroxide, the solution of the resultant soap decomposed by dilute sulphuric or hydrochloric acid, and the liberated fatty acid purified from the accompanying oleic acid by repeated crystallisation from hot alcohol, till the pressed crystals have a melting point of  $62^{\circ} C$ .<sup>1</sup> It is manufactured on a large scale by the reaction of potassium hydroxide upon oleic acid at a high temperature,

<sup>1</sup> Chittenden and Smith prepare palmitic acid from myrtle wax, which is said to contain only lauric acid in addition. By repeatedly crystallising the separated fatty acids from hot alcohol, pure palmitic acid, melting at  $62^{\circ}$ , is readily obtained.

or by saponifying palm oil and pressing the fatty acids obtained. The product is commonly, but improperly, called "palmitine."

Palmitic acid is a white substance, melting at 62° C. to a colorless oil, which solidifies on cooling to a white, finely crystalline mass. It is insoluble in water or dilute acids, but is soluble in alcohol, ether, carbon disulphide, hydrocarbons, and fixed oils. It cannot be distilled without decomposition under the ordinary pressure, even in the absence of air, but under a pressure of 100 mm. of mercury boils constantly at 268.5°, and distils practically unchanged.

Palmitic acid is but slightly soluble in cold alcohol. H€hner and Mitchell (*Analyst*, 1896, 323) have found 100 c.c. of methylated alcohol (94.4 per cent. by vol.) to dissolve the following quantities after being kept at 0° C. for the time stated.

NO. OF HOURS	GRAMS DISSOLVED	NO. OF HOURS	GRAMS DISSOLVED.
12	1.208-1.320	108	1.056
36	1.244	192	1.044
60	1.211	156	1.028
84	1.134		

The hot alcoholic solution has an acid reaction, and on cooling deposits the acid in tufts of small white needles.

Crystallisation from hot alcohol may be employed to separate palmitic acid from *oleic acid*, and, if repeated sufficiently often, from its lower homologues *myristic* and *lauric acids*. Mixtures of palmitic acid with certain proportions of myristic or lauric acid are, however, said to be incapable of analysis by fractional crystallisation from alcohol or ether. Mixtures of these homologous acids in certain proportions melt at a lower temperature than either acid separately. The method of ascertaining the composition of such mixtures, including those containing *stearic acid*, is described on page 241 *et seq*.

A method of separating palmitic acid from *oleic* and *linolic acids* and their homologues is given on page 246.<sup>1</sup> A method of separating palmitic and oleic acids, which is useful for analysing the product obtained by saponifying palm oil by the autoclave process, is described on page 262. Commercial palmitic acid may be examined in the same manner as stearic acid.

**METALLIC PALMITATES**—These present the closest resemblance to

<sup>1</sup> Chittenden and Smith (*Amer. Chem. Jour.*, vi, 217) find that the presence of free acetic acid increases the solubility of barium, magnesium, and lead palmitates in alcohol to such an extent as to render the separation of the acid in these forms incomplete. Further, the precipitates undergo partial decomposition when washed, either with water or with alcohol containing acetic acid.

the corresponding stearates (page 256 *et seq.*), and require but little separate description. Barium, magnesium, and lead palmitates are more readily soluble in alcohol, especially in presence of acetic acid than are the corresponding stearates.

Adipocere, a wax-like substance found in large quantity in corpses buried under certain conditions, is said to consist largely of palmitic acid mixed with potassium and calcium palmitates.

*Aluminium Palmitate* may be prepared in a manner similar to the corresponding oleate. It is an elastic amorphous mass, insoluble in water, but dissolving in petroleum spirit and oil of turpentine to form very viscous solutions which have found applications as varnishes. The film of aluminium soap left on evaporation retains its elasticity, and is odorless and impervious to water (see *J. S. C. I.*, 1882, 278). Aluminium palmitate has some practical interest as an ingredient of "oil pulp" or "thickener."

**PALMITIC ESTERS**—These present a close analogy to the corresponding stearates.

*Tridecyl Palmitates* or *Palmitins* are obtainable synthetically by means similar to those employed for the preparation of the stearins. Chittenden and Smith (*Amer. Chem. Jour.*, vi. 217) have given the following data —

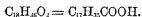
	MONOPALMITIN	DIPALMITIN	PALMITIN
100 parts of absolute alcohol, at 20-25° C., dissolve,	4.135	0.210	0.005
Appearance of fat deposited from alcoholic solution, .	Small spherules, showing no distinct crystalline form	Long curved needles	Groups of irregular crystals
Appearance of fat deposited from ethereal solution, .	Rhombic plates, either single or in branches	Warty masses	Irregular doubly curved bodies, single and crossed in groups
Melting point, °C.,	63.0	61.0	62-64
Solidifying point, °C.,	62.5	57.0	45.5-47

An isomeric modification of dipalmitin was obtained melting at 49° C. and solidifying at 47° to 48°. There was also obtained a very stable mixture of one part of palmitin with three of dipalmitin. This product crystallised from alcohol in bunches of needles, which melted at 68° to 69° and solidified between 64° and 67°.



**Stearic Acid.**

*French*—Acide stéarique. *German*—Stearinsäure; Talgsäure.



The triteryl ester of this acid occurs extensively in nature, especially in the harder fats of the animal kingdom, such as mutton and beef suet.

Stearic acid may be prepared pure by saponifying tallow with potassium hydroxide, decomposing the solution of the resultant soap with a dilute acid, and purifying the liberated fatty acids from oleic acid by crystallisation from hot alcohol. The pressed crystals consist essentially of a mixture of stearic and palmitic acids. It should be purified by recrystallisation, and 4 parts dissolved in such a proportion of hot alcohol that nothing will separate out on cooling to  $0^\circ$ . A solution of 1 part magnesium acetate in boiling alcohol is added and the liquid allowed to cool, when magnesium stearate will separate (page 241). The precipitate is filtered off, washed with cold alcohol, boiled with water and hydrochloric acid, and the purity of the resultant stearic acid proved by a careful determination of the melting point, which should be  $69.2^\circ \text{C}$ .

The commercial product commonly termed "stearine" really consists essentially of a mixture of free stearic and palmitic acids, and may be conveniently employed for the preparation of pure stearic acid, instead of tallow or other fat. The "stearine" may be at once dissolved in hot alcohol and the solution precipitated with magnesium acetate as above described. Commercial stearine often contains a considerable admixture of paraffin wax or other hydrocarbons, the absence of which should be proved before employing the substance for the preparation of stearic acid.

Shea-butter, when obtainable, may be conveniently employed as a source of stearic acid, as the fatty acids produced by its saponification consist solely of stearic and oleic acids, which can be separated perfectly by repeated crystallisations from hot alcohol.

Stearic acid presents the closest resemblance to palmitic acid, the following being the most tangible distinctions —

	PALMITIC ACID	STEARIC ACID
Melting point .. .. .	62 $0^\circ \text{C}$	69 $2^\circ \text{C}$
Boiling point, under 100 mm. pressure ..	268 $5^\circ \text{C}$	287 $^\circ \text{C}$
Solubility in cold absolute alcohol ..	9.3 per cent	2.5 per cent
Manner of crystallisation from alcohol ..	Tufts of small white needles	Naïveous laminae, or needles
Behavior with magnesium acetate .. ..	See page 241	See page 241.
Melting point of lead soap .. ..	108 $^\circ$ -112 $^\circ \text{C}$	125 $^\circ \text{C}$ .

In the analysis of natural oils and fats, the palmitic and stearic acids are usually obtained together, the oleic acid being separated by treating the lead soaps with ether, as described on page 246. In the mixture of palmitic and stearic acids thus obtained, the proportions of the two constituents can be approximately determined by one of the methods described on page 240 *et seq*, but the rigidly accurate analysis of such mixtures is not at present possible.

COMMERCIAL STEARIC ACID varies much in quality and appearance according to its source, but usually consists of a mixture of stearic acid with more or less palmitic and, sometimes, oleic acid. Hydrocarbons and unsaponified fat may also be present, but the proportion of these impurities is seldom large. The method of assay is similar to that employed for oleic acid, with the addition of a determination of the solidifying point by method *d*, page 37, from which the relative proportions of stearic and palmitic acids in the sample can be deduced; or, in the absence of hydrocarbons and unsaponified oil, the proportions of stearic and palmitic acids can be deduced from the results of the titration with standard alkali (page 242). The proportion of oleic acid may be ascertained by multiplying the iodine absorption by 1.11 (page 237).

METALLIC STEARATES.—Stearic acid forms a well-defined class of salts, all of which, with the exception of those of the alkali-metals, are insoluble in water, and mostly in alcohol and ether.

The stearates present very close resemblances to the palmitates, the chief tangible points of distinction being the more ready solubility of magnesium palmitate in alcohol and the different melting points of the lead salts. Lead palmitate melts at  $108^{\circ}$  according to Maskelyne, and between  $110^{\circ}$  and  $112^{\circ}$  according to Heintz, while lead stearate melts at  $125^{\circ}$ . Palmitates and stearates may also be distinguished by the melting points and combining weights of the liberated fatty acids.

*Potassium Stearate*,  $\text{KC}_{17}\text{H}_{35}\text{O}_2$ , may be prepared by saturating a hot alcoholic solution of stearic acid with alcoholic potash, using phenolphthalein as an indicator of the point of neutrality. On concentrating the solution and allowing it to cool, the potassium stearate crystallises in shining needles or laminae. It also separates on cooling a solution of 1 part of stearic acid and 1 of caustic potash in 10 parts of water. The opaque granules formed may be purified by crystallisation from alcohol. Or a boiling alcoholic solution of stearic acid may be mixed with an excess of a boiling aqueous solution of potassium carbonate, the liquid evaporated to dryness, the residue exhausted with

boiling alcohol, and the filtered solution allowed to cool, when crystals of potassium stearate will be deposited.

Potassium stearate dissolves in about ten times its weight of water at the ordinary temperature, forming a mucilaginous mass. On heating the solution it becomes clear, and if diluted with a large proportion of cold water an *acid stearate* of the composition  $\text{KC}_{18}\text{H}_{35}\text{O}_2, \text{HC}_{18}\text{H}_{35}\text{O}_2$  separates out in delicate, white, pearly laminæ, while a basic stearate remains in solution. An analogous decomposition by excess of water is suffered by other alkali-metal salts of the higher fatty acids, and is a leading cause of their application as soaps.

*Ammonium Stearate*,  $\text{NH}_4\text{C}_{18}\text{H}_{35}\text{O}_2$ , is obtained as a crystalline mass by incorporating strong ammonium hydroxide with melted stearic acid, and keeping the product over sulphuric acid till the excess of ammonia has evaporated. On further keeping in this manner, it gradually loses ammonia. (Wright and Thompson.)

*Sodium Stearate*,  $\text{NaC}_{18}\text{H}_{35}\text{O}_2$ , resembles the potassium salt, but is harder. It is decomposed in a similar manner, but with greater facility, by excess of water, and is less soluble in alcohol than potassium stearate. Sodium stearate may be separated from sodium palmitate by fractional crystallisation from hot alcohol.

*Barium and Calcium Stearates* are crystalline precipitates insoluble in water. The *magnesium* salt is similar, but soluble in boiling alcohol (see page 255).

*Lead Stearate*,  $\text{Pb}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$ , as prepared by double decomposition, forms a white amorphous powder, melting at  $125^\circ \text{C}$ . to a colorless liquid, which solidifies on cooling to an opaque amorphous mass. It is insoluble in water, alcohol, ether, or petroleum spirit. In these characters it is simulated by lead palmitate, myristate, arachidate, &c, but the lead salts of oleic acid and its homologues, as also of linolic and ricinolic acids, are soluble in ether and petroleum spirit.

**STEARIC ESTERS**—*Ethyl Stearate*,  $\text{C}_2\text{H}_5\text{C}_{18}\text{H}_{35}\text{O}_2$ , is prepared by passing hydrochloric acid gas into a solution of stearic acid in absolute alcohol. It is also formed by boiling tristearin with sodium ethylate, or with a quantity of alcoholic potash insufficient for its complete saponification. Ethyl stearate is a crystalline, easily fusible, wax-like solid, readily soluble in alcohol and ether, and boiling at  $224^\circ \text{C}$ . with partial decomposition.

*Triethyl Stearates* are obtainable synthetically by heating together, under pressure, suitable proportions of stearic acid and glycerol. Products containing either one, two, or three molecules of the stearic radicle are thus obtainable.

Monostearin and distearin do not appear to occur naturally, but *trityl tristearate* is identical with the stearin which, in admixture with palmitin, constitutes the less fusible portion of solid fats. For brevity, trityl stearate is frequently called "stearin." It is not identical with commercial "stearine," which is a mixture of free stearic and palmitic acids obtained by the saponification of the neutral fats.

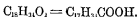
*Stearin* forms white, shining nodules, fine needles, or pearly laminae resembling spermaceti. It is tasteless, neutral, and volatile almost without decomposition in a vacuum. Heated to a high temperature, it decomposes and gives off an offensive odor of acrolein. It appears to exist in two isomeric modifications. As crystallised from ether it has a melting point of  $71.6^{\circ}$ . If the crystals so obtained be heated four degrees or more above the melting point, they are converted into a modification which solidifies to a waxy mass at  $52^{\circ}$  C and melts at  $55^{\circ}$ . If the latter be reheated a few degrees above the melting point, the original substance, melting at  $71.6^{\circ}$ , is obtained.

Stearin is insoluble in water and nearly insoluble in rectified spirit. In boiling absolute alcohol it dissolves freely, and is deposited in flocks on cooling. Stearin also dissolves readily in boiling ether, but the liquid retains less than 1 per cent. on cooling. It is readily soluble in fixed and volatile oils, and in carbon disulphide. When heated in a vacuum, it distils almost unchanged, but under the ordinary pressure it is decomposed with formation of carbon dioxide, acetic acid, water, free carbon, and olefins of boiling points ranging from  $190^{\circ}$  to  $245^{\circ}$ .

Pure stearin does not change on exposure to air at the ordinary temperature. When impure, it is liable to become rancid, apparently owing to the presence of olein. Stearin readily undergoes saponification when heated with alkalis or other strong bases, with formation of a metallic stearate and glycerol.

### Oleic Acid.

*French*—Acide oléique. *German*—Oelsäure.



Oleic acid is one of the most widely distributed fatty acids, occurring as an ester in most non-drying fixed oils, especially almond and olive oils, and in smaller proportion also in solid fats, such as lard, palm oil, butter, and goose fat.

For the preparation of pure oleic acid an oil rich in olein, as almond or olive oil, is saponified by alkali, the soap dissolved in water and decomposed by excess of dilute hydrochloric or sulphuric acid.

White Castile soap may be employed as the starting-point, thus saving the trouble of saponifying. The use of commercial oleic acid is not to be recommended, owing to the frequent presence of hydrocarbons. The liberated fatty acids are separated from the aqueous liquid, and heated for some time on the water-bath with about 1 part of finely ground lead monoxide for every 20 parts of oil taken for the operation. Excess of lead oxide should be avoided, as it occasions the formation of a basic oleate, which is subsequently treated with difficulty. The proportion of lead oxide prescribed is insufficient to combine with all the fatty acid, but the result is merely that a portion of the oleic acid remains in the free state, while the more powerful palmitic and stearic acids form lead salts.

The product is next treated with about twice its measure of ether, which dissolves the lead oleate and free oleic acid, and leaves the lead palmitate and stearate unchanged. The solution is separated from the insoluble salts, and hydrochloric acid added until the aqueous liquid has a strongly acid reaction even after shaking. The lower layer now contains lead chloride, while the ether retains the oleic acid. It is separated from the acid liquid, washed by agitation with water, and the ethereal layer removed and the ether evaporated off as rapidly and at as low a temperature as possible.

According to E. C. Saunders, rectified spirit may be advantageously substituted for the ether prescribed in the above process.

The oleic acid obtained by the foregoing process is apt to retain a little coloring matter and products of oxidation. To remove these, Biomeis recommends that it should be cooled below its solidifying point, and subjected to strong pressure between folds of filter paper. The residual oleic acid is melted, again cooled, and the purification by pressure repeated. Another method of purification consists in dissolving the oleic acid in ammonia, precipitating the solution by barium chloride, purifying the barium oleate by crystallisation from alcohol, and then decomposing it with tartaric or other suitable acid.

Pure oleic acid is a colorless, odorless, tasteless oily liquid, having a specific gravity of .897 at 19° C, and .876 at 100° C. When cooled to about 4° C it solidifies to a white crystalline mass, and on cooling its hot alcoholic solution is deposited in white needles, which melt at 14° C.

Pure oleic acid is not altered by exposure, and is free from acid reaction; but the impure substance gradually absorbs oxygen, becomes yellow, and acquires an acid reaction and a rancid taste and smell. The altered product has a lower melting point than the pure acid.

Oleic acid is much thinner than the neutral fixed oils, and is less liable to leave a greasy stain. When applied to the skin it wets it almost like water, and is very rapidly absorbed.

Oleic acid is insoluble in water, but dissolves with facility in alcohol, ether, carbon disulphide, chloroform, and hydrocarbons, and is also miscible with neutral fats and essential oils. The solution of oleic acid in alcohol usually has an acid reaction to litmus, a fact said to be due to the presence of impurities. It turns milky when largely diluted with spirit, but the turbidity disappears on adding a few drops of hydrochloric acid. Oleic acid dissolves in ammonium hydroxide and solutions of caustic alkalis to form oleates, from which others may be obtained by double decomposition.

Oleic acid may be distilled in a vacuum, or in a current of superheated steam at 250° C., without material alteration, but if distilled with contact of air it is partially decomposed, with formation of carbon dioxide, hydrocarbons, acetic, caproic, caprylic, capric, sebacic, and other acids.

SEBACIC ACID,  $C_{18}H_{34}O_4 = C_8H_{16}(COOH)_2$ , is also produced when oleic acid is *rapidly* heated with excess of caustic alkali. Its formation is a characteristic test for oleic acid and its immediate homologues. To detect it the alkaline residue should be treated with boiling water, and the liquid acidulated with acetic acid, again boiled, and filtered hot. The filtered liquid will, on cooling, deposit brilliant needles of sebacic acid, melting at 127° C., and soluble in 1000 parts of cold or 50 of boiling water.

When more strongly heated with caustic potash, oleic acid yields palmitate and acetate of potassium and free hydrogen, secondary products being also formed. The temperature necessary for this reaction is about 300° to 320° C. The process is commercially employed for the production of palmitic acid. The following formula expresses the main reaction which occurs.<sup>1</sup>—



Oleic acid combines with a molecule of bromine to form dibromostearic acid,  $C_{18}H_{32}Br_2O_2$ , as a yellow viscous oil having a fruit-like odor. Oleic acid also reacts in a perfectly definite manner with Hubl's reagent, and may be determined by that means.

<sup>1</sup> Small quantities of sebacic acid, caproic acid, caprylic alcohol and other bodies are also produced. The details of this process of manufacturing palmitic acid, for which nearly all fatty bodies, except mure's grease and suint fat, are available, have been described by W. Lant Carpenter (*J. S. C. I.*, 1883, 98).

Oleic acid is dissolved by concentrated sulphuric acid, a conjugate acid being formed which has been used in Turkey-red dyeing and calico-printing

Strong nitric acid oxidises oleic acid, with formation of acids of the acetic and oxalic series (including succinic acid)

By oxidation with potassium permanganate in presence of an excess of caustic potash oleic acid yields dihydroxystearic acid,  $C_{17}H_{33}(OH)_2 \cdot COOH$ , a crystalline body melting at  $136.5^\circ$ , and solidifying at  $119^\circ$  to  $122^\circ$ .

When oleic acid is heated to  $200^\circ$  or  $210^\circ$  C in a sealed tube with amorphous phosphorus and fuming hydriodic acid, it assimilates hydrogen, and is converted into stearic acid,  $C_{18}H_{36}O_2$ .

When the red fumes generated by acting on nitric acid by starch or arsenious oxide, or by a mixture of sulphuric acid and sodium nitrite, are passed for a short time into oleic acid carefully kept cold, the liquid gradually thickens, and in the course of an hour or so solidifies to a crystalline mass of an isomer of oleic acid called elaidic acid. It may be purified by agitation with boiling water, followed by crystallisation from alcohol.

ELAIDIC ACID,  $C_{18}H_{34}O_2$ , then forms large pearly plates, resembling benzoic acid, melting at  $45^\circ$ , and distilling almost unchanged. In the solid condition it is unchanged in the air, but in the fused state it readily absorbs oxygen, becoming yellow and pasty, and acquiring an odor like that of poppy oil. With bromine, fused potassium hydroxide, and phosphorus and hydriodic acid, elaidic acid behaves like oleic acid. Elaidic acid has a strong acid reaction, and forms a series of well-defined salts, all of which, if neutral, are said to be insoluble in water. *Sodium elaidate*,  $C_{18}H_{33}NaO_2$ , crystallises from alcohol in silvery laminae, and the *potassium* salt in glistening needles. The *barium* and *lead* salts are white precipitates.

The property of forming an isomer of higher melting point under the influence of nitrous acid is not peculiar to oleic acid. It is exhibited also by its olein, by its homologues hypogeic, deglic, and erucic acids, by ricinolic acid, but not by the fatty acids characteristic of the drying oils.

#### DETERMINATION OF OLEIC ACID

When occurring in the free state and unmixed with other acids, oleic acid may be conveniently and accurately determined by titration with standard alkali (page 104). In presence of acids of the stearic series it may be titrated with Hubl's solution, each 1 c.c. of decinormal

iodine absorbed corresponding to 0.0141 gm. of oleic acid. The determination of oleic in presence of linolic acid is described on page 237.

Oleic acid may be determined gravimetrically when in admixture with acids of the stearic series by utilising the solubility of its lead salt in alcohol, ether, or petroleum spirit, in the manner described for its preparation (page 259). The best method of applying the principle for analytical purposes is described on page 246.

According to F. Sear, palmitic and oleic acids can be separated by heating the mixture with excess of zinc oxide and digesting the product in the cold with carbon disulphide (see page 249).

A process for the separation of oleic and stearic acids has been devised by J. Daval. It is based on the solubility of oleic acid in a liquid containing certain proportions of alcohol, water, and acetic acid, and the insolubility of stearic acid in the same mixture. Whether palmitic acid behaves like stearic acid is not stated. The solvent is prepared by adding 22 measures of a mixture of equal volumes of glacial acetic acid and water to 30 measures of alcohol of 817 specific gravity. The correctness of this mixture is tested by agitating 5.2 c.c. with 1 c.c. of pure oleic acid. Complete solution of the latter should take place, and the fatty acid should wholly separate on adding 0.1 c.c. more of the mixture of equal volumes of acetic acid and water. If this separation does not take place, the proportions must be varied until the mixture is sufficiently sensitive. It is kept in a well-closed bottle, in contact with fine shavings of stearic acid.

The analysis is performed by treating 1 gm. of the sample of free fatty acids in a finely divided state with 16 c.c. of the solvent mixture. The tube is closed, agitated several times, and then set aside for 24 hours at a temperature not exceeding 15° C. The liquid is then filtered, air being excluded, and the residue is washed several times with the solvent mixture. The stearic acid can be dissolved off the filter with ether, and the oleic acid recovered from the solution by neutralising it, evaporating to a small bulk, adding hydrochloric acid, agitating with ether, and evaporating the ethereal solution at 100° C.

A method for the approximate estimation of oleic and solid fatty acids in tallow is described on page 172.

#### COMMERCIAL OLEIC ACID.

Commercial oleic acid is obtained by subjecting to hydraulic pressure the mixture of fatty acids produced by the saponification of tallow, palm oil, and similar fats. The expressed liquid, technically known as "red oil," contains a considerable quantity of palmitic and stearic acids, which separate out on keeping the red oil for some time at a low temperature.

When fats are saponified by the autoclave process, the products



often contain a considerable proportion of unsaponified fats. In consequence of the comparative facility with which palmitin and stearin are saponified, the unaltered fat consists chiefly or wholly of olein, which, owing to its low melting point, becomes concentrated in the oleic acid expressed from the crude product. Saponification under high pressure always tends to cause more or less decomposition of the higher fatty acids, and, when actual distillation has been resorted to, notable quantities of acetic, suberic, and sebacic acids are formed, and the two latter will remain with the oleic acid, together with certain hydrocarbons, apparently belonging to the paraffin series, which are always simultaneously produced.

Commercial oleic acid, which is frequently, but improperly, called "oleine," varies considerably in properties and composition. It is sometimes a clear liquid, ranging in color from dark brown to pale sherry, while other specimens are quite partly from separated solid fatty acids. By distillation in a current of steam, oleic acid may be obtained wholly free from color, but possessing an acid odor from the formation of decomposition products. Undistilled oleic acid usually retains an odor suggestive of its origin. The specific gravity is also variable, ranging from about .887 to .908, or even more, according to the proportions of hydrocarbons, neutral oils, and solid fatty acids which happen to be present.

*Mineral acids* are sometimes present in sensible quantity in commercial oleic acid. They rarely interfere with its applications, but if necessary may be detected and estimated as on page 104, or by titrating the alcoholic solution with alkali and methyl-orange.

The presence of an abnormal proportion of *oxidation and secondary products* of an acid character is indicated by agitating 50 c.c. of the oleic acid with 1 c.c. of a 10 per cent solution of ammonia and 50 c.c. of water. Both the oleic acid and the aqueous liquid should by this means be deprived of any acid reaction of litmus.

The presence of *palmitic or stearic acid* in commercial oleic acid may be detected by saponifying the sample with alcoholic potash, adding a drop of phenolphthalein solution, and then acetic acid, drop by drop, until the pink color is just destroyed. The liquid is then filtered, mixed with twice its weight of ether, and an alcoholic solution of lead acetate added. Any white precipitate may consist of stearate or palmitate of lead, and may be filtered off, washed with ether, decomposed with dilute hydrochloric acid, and the liberated fatty acids weighed. All ordinary commercial oleic acid will indicate the presence of foreign fatty acids when examined in this manner.

*Neutral fats* will be indicated by the gradual separation of oily drops when equal measures of the sample and of alcohol are heated to 25° C for some time, while a pure acid will give a clear solution when thus treated. A very delicate test for neutral fats in oleic acid is described on page 252.

The presence of neutral fixed oils or hydrocarbon oils can also be inferred from the diminished proportion of alkali required, when the sample is titrated as on page 105. Five gm. of pure oleic acid will require 35.47 c.c. of seminormal caustic alkali, corresponding to 19.9 per cent of KHO, and a combining weight of 282. Hence the percentage of *oleic acid* in the sample may be found by dividing the percentage of KHO required by 0.199. Any admixture of palmitic acid will *increase* the amount of alkali required.

The neutralised liquid resulting from the last process may be treated with a known amount of standard alcoholic potash, and examined by Koettstorfer's process, when each 1 c.c. of additional seminormal alkali neutralised will indicate the presence of 0.145 gm. of *neutral fixed oil* in the sample.

The liquid left after the second titration may be evaporated with a further quantity of alcoholic potash, the residual soap dissolved in water, and the solution agitated with ether, as described on page 113. The ethereal solution is then separated and evaporated, and the *unsaponifiable matter* weighed.

In the case of an oleic acid obtained by distillation of an ordinary fat with superheated steam, the unsaponifiable matter or ether-residue obtained in the last process consists of *hydrocarbons* presenting the closest resemblance to those contained in the lubricating oils manufactured from petroleum and bituminous shale. Hence no means exist at present by which an intentional addition of a moderate proportion of hydrocarbon oil to oleic acid can be positively detected. According to the experience of the author, the hydrocarbons normally present in distilled oleic acid range from 3 to 7 per cent., and therefore any proportion notably in excess of the latter figure may be attributed to an intentional sophistication of the product with mineral or shale oil. The addition of these adulterants to oleic acid is extensively practised, although their presence greatly reduces the suitability of the oleic acid for one of its most important applications, which is that of greasing wool during the process of spinning. Any admixture of hydrocarbons reduces the property of ready saponifiability for which oleic acid is chiefly valued.

The foregoing statement respecting the proportion of unsaponifiable

matter present in distilled oleic acid applies to a product obtained by saponifying pure substances. Wool grease and the grease obtained by treating with acid the soapy liquors in which wool has been washed are much more impure articles. Besides the *hydrocarbons* formed on distilling such greases, the distilled product is liable to contain *actual* petroleum or shale products used in the wool-spinning, either intentionally or as adulterants of other oils, *petroleum* employed for antiseptic purposes on the living sheep, and *cholesterol* and other unsaponifiable matters contained in the "suint" or wool fat. Hence, an estimation of the "unsaponifiable matter" in such low-class oleic acids cannot be regarded as a reliable indication of the extent to which they have been adulterated by an actual addition of hydrocarbon oil. Some indication of the origin of the unsaponifiable matter may be obtained by treating the ether-residue with thrice its volume of rectified spirit, when the measure left undissolved may be regarded as indicating roughly the hydrocarbons present, while the cholesterol and solid alcohols from sperm or bottlenose oil pass into solution. (See "Wool Fat.")

The following table exhibits results obtained in the author's laboratory by the examination of specimens of commercial oleic acid of very different qualities. The "free fatty acids" were determined by titration with standard alkali, and calculated to their equivalent of oleic acid; but in the case of the semi-solid samples containing much palmitic acid the result thus obtained is necessarily in excess of the truth. The percentage of ether-residue shows the "hydrocarbons, &c.," in the samples, while the esters were in some cases determined indirectly, in other cases calculated from the result of Koettstorfer's saponification process, and in others deduced from the difference between the free fatty acids of the original sample and the total fatty resulting from its saponification. The samples and ether-residues to which an *f* is affixed were noted as being distinctly fluorescent —

	A	B	C	D	E	F	G	H	I
Condition, .	Clear	Clear	Fluid, with slight deposit	Semi-solid	Semi-solid	Consistent much solid		Fluid	Clear
Color, . . .	Pale brown	Pale brown, <i>f</i>	Brown	Brown	Pale brown	Pale brown, <i>f</i>			Sherry brown, <i>f</i>
Specific gravity,	8906		9055	9085	9014	9087		8904	9083
Free fatty acids,	96.3	91.8 <i>f</i>	80.3	87.7	96.2	84.5	89.4	77.2	65.3
Hydrocarbons, &c	1.3	3.9 <i>f</i>	2.2	2.9	4.8 <i>f</i>	10.1	2.0	26.8	35.9 <i>f</i>
Esters, direct, .				11.4		3.3			11.6
" by difference,	2.5	2.3	17.6	17.0		2.0	8.6	4.0	8.8

The first four samples were manufactured by the autoclave process, A and C being derived from tallow. E and F were probably autoclave products, the latter being of French manufacture. G was obtained from tallow by lime-saponification, and H and I were probably distilled oleins from recovered grease.

Grauvau and Valser (*J. Pharm. Chim.*, 1889, 232) have drawn attention to the fact that commercial oleic acid is sometimes adulterated with the acids from linseed oil. Such samples have a specific gravity of from 0.912 to 0.919 and do not dissolve completely in nine measures of rectified spirit. Shaken with an equal volume of sodium hydroxide solution, the mixture turns intensely yellow, pure oleic acid becomes grey. If the linseed oil acids be present in considerable proportion, they may be detected by the high iodine number. Hazura (*J. S. C. I.*, 1889, 641) adopts the following method.—50 gm. of the sample are saponified on the water-bath with dilute alcoholic potassium hydroxide. The potash soap is freed from alcohol and dissolved in 1000 c.c. of water. This strong alkaline solution is gradually mixed with 1000 c.c. of a 5 per cent. solution of potassium permanganate. After  $\frac{1}{2}$  to 1 hour, the manganese oxide is filtered off, the filtrate acidified with sulphuric acid, and again filtered. The filtrate thus obtained is neutralised with potassium hydroxide, concentrated to about 300 c.c., and again acidified with sulphuric acid, which produces a precipitate. The acid liquid, without removing the precipitate, is shaken with ether. If the precipitate dissolves in ether, it consists of azelaic acid ( $C_9H_{16}(COOH)_2$ ) and the original oleic acid is free from linseed-oil acids. If it does not dissolve, it is filtered off, recrystallised several times from water or alcohol, with the addition of animal charcoal, and, after air-drying, its melting point determined. If this be above  $160^\circ C$ , linseed-oil acids are undoubtedly present.

#### SULPHURIC ACID

When a non-drying fixed oil is cautiously treated with strong sulphuric acid, complex reactions occur, the precise nature of which depends on the conditions of the experiment. P. Juillard (*J. S. C. I.*, 1894, 520) states that olein treated in the cold with sulphuric acid yields two acids,—one monobasic, the other dibasic,—which appear to be addition products of sulphuric acid and olein. They are soluble in water. Oleic acid treated with sulphuric acid produces at first hydroxystearosulphuric acid,  $H(HSO_2)C_{18}H_{34}O_4$ , from which is formed hydroxystearic acid,  $HC_{18}H_{34}(HO)O_2$ .

**METALLIC OLEATES**—These form a well-defined series of salts,

many of which have received practical applications. They may be obtained by dissolving the metallic oxide of which the oleate is required in warm oleic acid; but such a method does not give compounds of very definite composition. A preferable plan is to precipitate an aqueous solution of sodium oleate with a neutral solution of the salt of the metal of which the oleate is required. Zinc, aluminium, iron, lead, copper, bismuth, and other oleates, are readily obtained in this way, and have received considerable application in medicine.

These oleates are readily analysed by agitating them with ether and a dilute mineral acid, which should be sulphuric, hydrochloric, or nitric, according to the metal present. The metals pass into the dilute acid liquid, and may be determined by the ordinary methods of mineral analysis. The oleic acid formed from the oleate is dissolved by the ether, and may be weighed after evaporating off the solvent. Any free oleic acid, neutral fat, or hydrocarbon (*e.g.*, vaseline) which may have been present in the original substance will also be found in the ether-residue, and may be determined by the methods indicated on page 104 *et seq.*

With the exception of the salts of the alkali-metals, all the metallic oleates are insoluble in water, though they dissolve in many instances in alcohol, ether, carbon disulphide, and petroleum spirit. The oleates of calcium, magnesium, and iron also dissolve in glycerol.

*Potassium Oleate*,  $\text{KC}_{18}\text{H}_{35}\text{O}_2$ , is the principal constituent of soft soap. It is a white, friable, deliquescent substance, which with a small quantity of water forms a transparent jelly, soluble in alcohol or a moderate quantity of water; but decomposed on copious dilution into free alkali and a gelatinous *acid oleate*, insoluble in water but readily soluble in alcohol (see page 270).

*Sodium Oleate*,  $\text{NaC}_{18}\text{H}_{35}\text{O}_2$ , is a constituent of hard soap. It may be prepared pure by neutralising an alcoholic solution of oleic acid with caustic soda and evaporating off the alcohol. It may also be obtained by the addition of sodium carbonate to hot oleic acid. It is not deliquescent, but by contact with air becomes gelatinous. Pure sodium oleate may be obtained in crystals from its solution in absolute alcohol, but not from aqueous alcohol or from the syrupy solution in water.

*Ammonium Oleate* is obtained in solution by treating oleic acid with cold aqueous ammonia. It is a gelatinous substance, soluble in water, and readily decomposing into ammonia and oleic acid.

*Barium Oleate*,  $\text{Ba}(\text{C}_{18}\text{H}_{35}\text{O}_2)_2$ , is a light crystalline powder, insoluble in water, and difficultly soluble in boiling alcohol.

*Magnesium Oleate*,  $Mg(C_{18}H_{33}O_2)_2$ , is insoluble in water, but soluble in alcohol and petroleum spirit.

*Aluminium Oleate* is a soft, white, putty-like substance, insoluble in water, but soluble in ether and petroleum spirit. It has received a curious application, owing to its great tenacity and peculiar property of stretching into a thin string without breaking. It is made by saponifying whale, cottonseed or lard oil with caustic soda, and adding the aqueous solution of the resulting soap gradually to a solution of alum. A tough, gummy precipitate of aluminium oleate, palmitate, &c, is formed, which constitutes the product known as "oil pulp." This may be dissolved in four or five times its weight of mineral lubricating oil to form "thickener," which is employed to impart a factitious viscosity to oil.<sup>1</sup> Such oil will readily form threads in dropping, and has a thick, glairy character. The false viscosity thus produced cannot be regarded as really increasing the lubricating value of the oil, and the use of aluminium soap for the purpose can only be regarded as an adulteration.

*Ferric Oleate* is dark red, but otherwise resembles the aluminium soap.

*Cupric Oleate* is a dark-green, wax-like substance, readily obtained by double decomposition. It becomes quite fluid at  $100^\circ$ , and dissolves with green color in all proportions of alcohol, ether, and fixed oils.

*Lead Oleate*,  $Pb(C_{18}H_{33}O_2)_2$ , is the principal constituent of the "lead plaster" of pharmacy. As obtained by double decomposition it is a light white powder, melting at  $80^\circ$  to a yellow oil, and solidifying on cooling to a brittle translucent mass. Lead oleate is quite insoluble in water, but soluble in alcohol and in ether, especially when hot. It is also dissolved by oil of turpentine and by petroleum spirit, the hot saturated solution in the last solvent solidifying to a gelatinous mass on cooling. The solubility of lead oleate in ether is utilised in analysis for the separation of oleic from palmitic and stearic acids.

<sup>1</sup> A sample of "oil-pulp," the analysis of which is given in the *Oil and Colourman's Journal*, vol. IV, p. 403, had the appearance of thick gelatin or soaked glue. It had a specific gravity of .921, and is said to have contained —

	Per cent
Paraffin oil of 966 specific gravity, . . . . .	48
Lard oil (uncombined), . . . . .	15
Fatty acids, 50 } . . . . .	36
Alumina, 5 } . . . . .	
Water, soda, and loss, . . . . .	1
	<hr/> 100

By boiling oleic acid with water and excess of lead oxide or basic lead acetate, a basic oleate is obtained which is nearly insoluble in ether.

*Zinc Oleate* is a white unctuous powder, soluble in carbon disulphide and petroleum spirit.

Many of the so-called commercial "oleates" are prepared by the use of Castile soap instead of pure sodium oleate. They are better described as "oleo-palmitates," and for pharmaceutical purposes are probably equally suitable.

#### OLEIC ESTERS

*Ethyl Oleate*,  $C_2H_5C_{18}H_{33}O_2$ , is prepared by passing dry hydrochloric acid gas into a solution of oleic acid in three times its measure of absolute alcohol. Etherification takes place very rapidly, and the ester separates from the liquid as an oily layer. It has a specific gravity of .870 at  $18^\circ$ , is soluble in alcohol, and is decomposed by distillation. Nitrous acid and its equivalents slowly convert it into the isomeric ethyl elaidate.

*Dodecetyl Oleate* and its *homologues* are said to constitute the greater part of sperm and bottlenose oils.

*Tritenyl Oleates* are obtainable synthetically by heating oleic acid and glycerol together in sealed tubes to about  $200^\circ$  for 24 hours. With excess of glycerol the monoolein,  $C_3H_5(OH)_2C_{18}H_{33}O_2$ , is produced. With excess of oleic acid, *olean*,  $C_5H_{11}(C_{18}H_{33}O_2)_2$ , is formed, and under special conditions the dioleate is said to be obtainable. Monoolein and diolein are not known to occur naturally, but olein occurs in many fixed oils, and may be obtained approximately pure by agitating olive or almond oil with a cold concentrated aqueous solution of caustic soda, which, it is said, saponifies the palmitin and leaves the olein mostly unchanged. After twenty-four hours, water is added and the soap solution separated from the oily layer, which should be washed with dilute alcohol and filtered through animal charcoal. As thus prepared, olein is a colorless, tasteless oil, readily soluble in ether or in absolute alcohol, and of a specific gravity between .900 and .920. By treatment with nitrous acid it is converted into solid elaidin. It solidifies below  $0^\circ$ , can be distilled in a vacuum, and on exposure to air oxidises and becomes acid.

## SOAPS.

By the term soap is commonly understood the various commercial products obtained by the action of alkalis on fats and oils; but the word is sometimes used in a more extended sense, so as to include all compounds produced by the substitution of metals for the hydrogen of the higher fatty acids

It has already been explained (page 42) that the great majority of the various solid and liquid fats consist of the tritenyl esters of the higher fatty acids, and that by treatment with strong bases, such as the alkalis, these yield glycerol and salts of the fatty acids, which last constitute essentially the "soaps"

The fatty acids which play the most important part in the formation of ordinary soaps are necessarily those which are the main constituents of the fatty oils used, the chief being lauric, palmitic, stearic, oleic, linolic, and ricinolic acids. Of late years the employment of previously prepared fatty acids has to some extent replaced the use of the natural oils and fats. Much soap is prepared in part with colophony or rosin, which consists essentially of a mixture of pinic, sylvic, and colophonic acids, with more or less pimaric acid and abietic anhydride

The bases used for producing commercial soaps from fatty acids or fats are exclusively potash and soda, as the soaps of the alkali-metals are alone soluble in water<sup>1</sup>. The bases are sometimes used separately and in other cases in admixture. The characters of the pure potassium and sodium salts of the more important fatty acids have already been described

Potassium soaps are deliquescent and have a low fusing point. Sodium soaps are mostly solid and hard at the ordinary temperature, and in the absence of free alkali are not deliquescent. Both forms are readily soluble in hot water and alcohol; their concentrated solutions solidify to a jelly on cooling. "Opodeldoc" is this jellied soap mixed with alcohol. Copious dilution of a solution of soap with cold water, or the cooling of a hot dilute solution, causes the precipitation of an acid soap, while free alkali or a basic soap remains in solution. This reaction has an intimate relation to the detergent properties of soap. Wright and Thompson (*J S C I.*, iv 630) investigated the extent to which neutral soaps of different kinds undergo hydrolysis by

<sup>1</sup> When in solution in water, potassium and sodium soaps are practically insoluble in ether, benzene, petroleum spirit, or carbon disulphide. Hence these solvents may be employed to separate them from unsaponified oil, free fatty acids, and hydrocarbon oils



treatment with water, and obtained the results shown in the following table —

NATURE OF SOAP	FATTY ACIDS		PERCENTAGE OF TOTAL ALKALI SET FREE BY ADDITION OF $x$ MOLECULES OF WATER TO ONE MOLECULE OF ANHYDROUS SOAP				
	Nature	Mean Molecular Weight	$x=150$	$x=250$	$x=500$	$x=1000$	$x=2000$
Sodium stearate,	Pure stearic acid	284	0.7	1.0	1.7	2.6	3.55
Sodium palmitate,	Neatly pure palmitic acid	256	1.45	1.9	2.6	3.15	3.75
Sodium oleate, . . .	Pure oleic acid	282	1.85	2.6	3.5	5.2	6.65
Coconut oil soap, . . .	Crude lauric acid	193	3.75	4.5	5.4	6.45	7.1
Caster oil soap, . . .	Crude ricinolic acid	291	1.55	2.2	3.0	3.8	4.5
Cottonseed oil soap (chiefly), . . .		260	2.25	3.0	5.0	7.5	9.5
Tallow and rosin soap (primrose), . . .		280	1.5	2.2	3.1	4.2	5.3
Tallow and palm oil soap,		271	1.1	1.55	2.6	4.1	5.3

It appears from this table that the tendency of the sodium soaps of lauric, palmitic, and stearic acids to undergo hydrolysis decreases with an increase of the molecular weight. The figures for tallow-rosin soap show that the presence of rosin soap does not materially affect the rate of hydrolysis of sodium oleate and stearate. The presence of free alkali causes a marked reduction in the extent of hydrolysis produced by a given amount of water. Thus, the tallow rosin soap, in presence of an amount of caustic soda equal to 15 per cent. of the alkali existing as soap, underwent no decomposition by 150 molecules of water, only 0.1 by 250, and 1.3 by 2000 parts of water.

The conclusions of C. Rotondi (*Chem. Review*, xiv, 228) are not wholly in accordance with those quoted above. Rotondi finds that water, especially when hot, decomposes neutral soaps into basic and acid soaps without the formation of free alkali. Basic soaps dialyse easily, are completely soluble in cold water, and are precipitated by brine without decomposition. They act as solvents for the acid soaps and free fatty acids, and emulsify fats without saponifying them. Carbonic acid renders basic soaps insoluble without the formation of free alkali; on warming the liquid re-solution takes place. Acid soaps diffuse with difficulty, are insoluble in cold water and but little soluble

in water, but are soluble in warm solutions of basic soaps. Acid soaps do not dissolve or emulsify either fatty acids or fats. See also M. Dechan and T. Mahen on basic soaps (*Pharm Jour* [3] xv. 1025).

The experiments of Krapps and Stern (*Beichte*, 1894, 1747) seem to prove that hydrolysis increases with the molecular weight of the fatty acids. This conclusion is directly opposed to that of Wright and Thompson, noted above.

The soaps of commerce may be divided broadly into two classes—*hard* and *soft*. Hard soaps are made with solid animal fats, vegetable fat oils, or free oleic acid and soda; for soft soaps, fish oils or vegetable drying oils are used, saponification being effected with potash. Hard soaps may be obtained with potash, provided a solid fat be employed, but a potassium soap is always softer than a sodium soap produced from the same fat. The hard soaps of commerce usually consist essentially of the sodium salts of the fatty and resin acids of the materials, the excess of alkali and the glycerol having been separated, but in the case of soft soaps no such separation is attempted, the whole being boiled down together. Hence soft soaps are more caustic than hard soaps, and contain various impurities. The solid white granulations or “figging” often seen in soft soap consist of potassium stearate, and to produce them a small quantity of tallow is used in the manufacture. As the figging is commonly but erroneously regarded as a proof of quality, it is sometimes imitated by an admixture of starch.

The soaps of commerce are arranged by W. Lant Carpenter (*Soap and Candles*, page 146) in the following classes, according to their method of production.—

1. Soaps produced by the direct union of free fatty acids and caustic alkali, or by the decomposition of alkali-carbonates by fatty acids.

2. Soaps produced by acting on a neutral fat by the precise quantity of alkali necessary for saponification, without the separation of any waste liquid, the glycerol produced by the reaction being retained by the soap. This class includes (a) soaps made by the cold process, and (b) soaps made under pressure.

3. Soaps produced by the ordinary method of boiling in open vessels, working with indefinite quantities of alkaline lye, the processes being controlled by the experience of the operator. The soaps of this class may be subdivided into (a) soft soaps, in which the glycerol is retained, potash being the base; (b) the so-called “hydrated” soaps, with soda for the base, in which the glycerol is retained, and of which “marine soap” may be taken as the type, and (c) hard soaps, with soda as a base, in which the glycerol is eliminated by addition of ex-

cess of brine or alkaline lye, comprising three kinds,—curd, mottled, and yellow soaps

The so called "cold process" of soap-making consists in mixing the fat, previously melted at as low a temperature as possible, with just sufficient soda lye (at about the same temperature) to effect complete saponification. The process has the advantage of being simple, and is often employed for the manufacture of the cheaper kinds of toilet soap, since the low temperature employed prevents dissipation of the perfumes added, but the saponification is apt to be incomplete, the product often containing both free alkali and unsaponified oil, besides which only the purest materials are available, as the whole of the glycerol and extraneous matters are retained in the final product. Transparent toilet soaps made by the cold process are liable to contain a considerable proportion of free alkali and sugar.

"Marine soap," so called from its valuable property of forming a lather with sea-water, is made by boiling palmnut or coconut oil with soda lye of 1.163 specific gravity. The alkali is added gradually until the presence of a faint excess is indicated by the taste. It is often difficult to cause saponification to commence, but once begun it proceeds with extraordinary rapidity, the mixture swelling up almost instantaneously to many times its volume. Additions of salt or brine, of sodium silicate, and of sugar are often made to this class of soap, samples of which may contain 70 per cent. of water.

Sodium stearate suffers no marked change in contact with 10 parts of water, while potassium stearate is converted into a thick paste or viscid solution. Sodium and potassium palmitates closely resemble the corresponding stearates. Sodium oleate is soluble in 10 parts of water and potassium oleate in 4 parts, forming a jelly with half this proportion. The consistency or hardness of soap is not dependent solely on the base present, but is greater in proportion to the stearin and palmitin preexistent in the oil, and less in proportion to the olein in it.

Sodium soaps are soluble in water, but insoluble in brine and other strong saline solutions. When a moderately strong solution of hard soap is precipitated by addition of common salt, the composition of the separated soap is unchanged, but from very dilute solutions acid soaps are thrown down (see page 270). Potassium soap cannot be separated in a similar manner by adding potassium chloride to its solution; while, if common soap be added to the solution of a potassium soap the precipitate consists of a sodium soap, an equivalent amount of potassium chloride being formed in the solution. Concentrated solutions of

caustic alkali and alkali-carbonates also separate either potassium or sodium soap from its solution, but in weak alkaline lyes soap is readily soluble. Coconut and palmnut oil soaps consist largely of sodium laurate, and require a much larger proportion of salt to separate them from their solutions than is the case with any other varieties. Hence their use on board ships, as they form a lather with sea-water. The property possessed by common salt of precipitating soap from its aqueous solution is extensively employed for separating soap from the glycerol, excess of water and alkali, and impurities in the materials used.

The oils and fats employed by the soapmaker are very numerous, the greater number of those classified in the tables commencing on page 91 doing duty in some form or under special circumstances. Besides the actual esters or neutral oils, the free fatty acids obtained by saponifying palm oil, coconut oil, tallow, and other fatty oils are largely used, as are the fatty acids obtained from cottonseed oil and recovered grease. Tallow is largely employed as such, but is superseded to some extent by palm oil. Castor oil is extensively employed for making transparent toilet soaps. Lard soap is very white, solid, inodorous, and very valuable for toilet use. Cottonseed oil is now employed to a large extent for soap-making. Hempseed oil, saponified with potash, is also much used for making soft soap. The product is green, pasty, and so soft that the least addition of water renders it liquid. Ordinary "yellow soap" is usually made by saponifying tallow or palm oil with soda. More or less resin is always added, but the use of too large a proportion renders the soap dark, soft, too readily soluble, and too strongly caustic. Soaps made from the drying oils are usually soft and flabby, and those from fish oils commonly betray their origin by their odor.

From what has hitherto been stated it might be assumed that commercial soaps consist solely of the hydrated potassium or sodium salts of the fatty and resin acids, with or without the glycerol produced by the saponification. In practice this is far from being the case; for, in addition to the above-named constituents, soaps are necessarily liable to contain more or less unsaponified oil or uncombined fatty acids on the one hand, and excess of alkali on the other.<sup>1</sup> The latter may exist either as caustic alkali or as an alkali-carbonate, in addition to which there may be sulphates, chlorides, or silicates, and traces of

<sup>1</sup> C R Alder Wright has proposed the addition of ammonium salts, such as the sulphate or chloride, in quantity sufficient to react with the free alkali which is so objectionable an ingredient of toilet soaps.

calcium, magnesium, aluminium, and iron compounds existing as impurities in the alkali used, common salt as a result of the precipitation of the soap with brine, and, in transparent toilet soaps, alcohol. The use of alcohol for purifying toilet soaps has the advantage of separating alkali-carbonates and neutral salts, but any caustic alkali dissolves with the soap. On subsequently evaporating the alcohol, the soap remains as a more or less translucent mass, the transparency of which can be further increased by an addition of glycerol or loaf-sugar, the latter substance sometimes being present in large proportion in so-called "glycerin soaps," from which glycerol is wholly absent.

Besides the foregoing accidental impurities, legitimate additions are frequently made to soap. Thus, potassium and sodium carbonates are added to "cold-water soap" to communicate the power of lathering readily with hard water, and to increase the detergent properties generally, sodium silicate is often added to soap intended for manufacturing uses and, though objectionable in some cases, must be considered a legitimate addition in others. Sodium aluminate is sometimes employed, and borax, which itself possesses detergent properties of a marked character, is also used. Petroleum naphtha to the extent of 10 per cent is sometimes incorporated with soap. It is said to increase the detergent action. A soap of this kind, now largely sold in the United States, is prepared by mixing the petroleum product with a rosin soap-mass and adding this to a common soap.

Small proportions of various substances are also added to soap as coloring and perfuming agents. Mottling is produced by iron salts, ochre, ultramarine, or even more objectionable matters, such as vermilion and copper arsenite. Such additions remain as a residue on dissolving the soap in water or spirit, and should never exceed 1 per cent even in mottled soap, and should be less in other varieties. The perfuming agents are mostly used in very small quantities, and are perfectly ineffective for good or evil, and in some of the medicated soaps the additions to which the alleged therapeutic properties of the soap are attributed are present in such small proportion that the same remark is applicable.

Medicated soaps are now sold which contain a considerable proportion of agents, for which more or less curative value is claimed. Among these may be enumerated carbolic and cresylic acids, thymol, naphthalene and creosote oils, petroleum, vaseline, camphor, and gelatin.

A number of insoluble and inert organic and inorganic substances are added to soap, either with the alleged object of imparting special

characters, or manifestly to act the part of "filling" or adulterants. Among these may be enumerated oatmeal, bran, sawdust, barium sulphate, steatite, china-clay, pipe-clay, fuller's earth, sand, pumice-stone, kieselguhr, chalk, and whiting. Dr. Leffmann found 33 per cent of mineral matter in a sample of red Castile soap. The so-called "sand soaps" now largely used for scouring purposes are usually mixtures of common soap, containing much rosin and some free alkali, with finely pulverised quartz. The proportion of quartz is often over 80 per cent. Diatomaceous earth is also used. In a sample of a much advertised soap, said to contain milk and sulphur, neither of these bodies was found, but there was much china-clay and a notable amount of free alkali.

### Assay and Analysis of Soaps.

In analysing soaps care must be taken to obtain a fairly representative sample. In the case of hard soaps this is best effected by cutting a transverse slice from the middle of the bar or cake. A cylinder withdrawn from a cake by means of a cork-borer or cheese-sampler also affords a fairly good sample. In many cases it is necessary to reduce the soap to thin shavings or slices, which should be thoroughly mixed by shaking, and preserved in a well-closed bottle.

A COMPARATIVE ASSAY of different soaps can be effected in a useful and simple manner by ascertaining what measure of a standard solution of the sample must be added to a 50 c.c. of a very dilute solution of calcium chloride or sulphate solution in order to obtain a persistent lather on shaking. The soap solution is made by dissolving 10 grm. of the sample in proof spirit (sp. gr. 920), filtering, and diluting the filtrate with proof spirit to 1 litre. The test is made exactly as in determining the hardness of waters, the soap solution being added to the standard hard water in small quantities at a time until a lather is obtained on shaking, which remains for at least five minutes when the bottle used for the operation is placed on its side. The standard hard water may conveniently be prepared by exactly neutralising 40 c.c. of decinormal sulphuric or hydrochloric acid by cautious addition of lime-water, and diluting the solution to 1 litre, when it will have a hardness of 14 degrees of Clark's scale.

# OUTLINE OF SYSTEMATIC SCHEME FOR ANALYSIS OF SOAPS

<p><b>A</b>—Dry 10 gm of the soap as described on page 273. The loss is <i>not</i> a trace of alcohol and essential oils. Place the dried soap in a beaker and add 10 ml of distilled water. Boil for 10 minutes, then add 10 ml of 95% alcohol. Boil for 10 minutes more. Filter and evaporate the alcohol. The residue is the soap. It is not suitable unless it has been redissolved with caustic alkali.</p>	<p><b>C</b>—Residue. After the adhering petroleum spirit is evaporated, and the previous drying and treatment with boiling water. In some cases omitted, in which case 10 gm of the soap is used. The residue is dried in water, and the solution shaken with petroleum spirit, if desired. The aqueous solution is filtered, decanted, or strained from any insoluble matter.</p>	<p><b>H</b>—Residue. Consists of <i>insoluble matter</i>, mineral and organic. It may be dried in water, instead of, and in a manner similar to, Residue N.</p>	<p><b>L</b>—Residue. Treat the hot liquid with a known amount of standard sulphuric acid, using a moderate excess. Boil for 10 minutes, then filter through a filter (see page 285).</p>	<p><b>I</b>—Exhaust 10 gm of the sample with 100 to 150 cc of neutral rectified spirit, or, preferably, absolute alcohol, and evaporate to dryness. The residue is not suitable unless it has been redissolved with caustic alkali.</p>	<p><b>N</b>—Residue. Consists of <i>insoluble matter</i>, mineral and organic. It may be dried in water, instead of, and in a manner similar to, Residue N.</p>
<p><b>B</b>—Solution. Their total amount may be determined by distilling the whole or an aliquot part of the solution, drying the residue at 100° C., and weighing.</p>	<p><b>D</b>—The aqueous solution is filtered, decanted, or strained from any insoluble matter.</p>	<p><b>G</b>—Oil layer. Consists of <i>fat</i>, <i>oil</i>, and <i>residue</i>. It may be treated as described on page 289.</p>	<p><b>F</b>—Solution. Add methyl orange and turn the color to yellow. The difference between the previously added and the equivalent of acid required to neutralize the total sample is the amount of free alkali in the unsaturated liquid as on page 288.</p>	<p><b>J</b>—Add methyl orange and turn the color to yellow. The difference between the previously added and the equivalent of acid required to neutralize the total sample is the amount of free alkali in the unsaturated liquid as on page 288.</p>	<p><b>K</b>—Solution. Dry at 100° C and weigh (see page 291). Exhaust thoroughly with boiling water, and filter, decant, or strain.</p>
<p><b>E</b>—Solution. Add methyl orange and turn the color to yellow. The difference between the previously added and the equivalent of acid required to neutralize the total sample is the amount of free alkali in the unsaturated liquid as on page 288.</p>	<p><b>M</b>—Solution. Divide into two equal parts (see page 294).</p>	<p><b>1</b>—Add methyl orange and turn the color to yellow. The difference between the previously added and the equivalent of acid required to neutralize the total sample is the amount of free alkali in the unsaturated liquid as on page 288.</p>	<p><b>2</b>—Examine for borate, silicate, phosphate, and sulphate as described on page 294.</p>	<p><b>3</b>—Add methyl orange and turn the color to yellow. The difference between the previously added and the equivalent of acid required to neutralize the total sample is the amount of free alkali in the unsaturated liquid as on page 288.</p>	<p><b>4</b>—Add methyl orange and turn the color to yellow. The difference between the previously added and the equivalent of acid required to neutralize the total sample is the amount of free alkali in the unsaturated liquid as on page 288.</p>

From the preceding list of the numerous substances occurring as frequent or occasional ingredients of commercial soaps, it is evident that the complete analysis of soap is sometimes a difficult and tedious operation. In the great majority of cases, however, the examination may be restricted to a determination of the leading constituents, and of these some have a greater or less importance according to the purpose for which the soap is intended to be used.

*Manufacturers' Soaps* should be tested for the proportions of water, total alkali, and crude fatty acids, while the percentages of caustic alkali, alkali-carbonate and silicate, combined fatty and resin acids, and free fatty acids and unsaponified oil are secondary determinations which are frequently of considerable importance.

*Household and Laundry Soaps* should be tested for the proportions of water, alkali as soap, alkali in other forms, and total fatty acids. Phenol should also be determined in soap said to contain it.

*Toilet and Fancy Soaps* should be tested for water, alkali as soap, alkali in other forms, fatty and resin acids, glycerol, sugar, and insoluble matters.

*Medicated Soaps* should be specially examined for the proportion of the active or quasi-active constituent said to be present, such as phenol, sulphur, thymol, tar, and vaseline.

The table on page 277 exhibits a systematic scheme for the complete analysis of even a complex soap. It is mainly based on the scheme drawn up by C. R. Alder Wright and C. Thompson, which is a modification of that of A. R. Leeds, who appears in great measure to have derived his method from the first edition of this work. With the subsequent detailed instructions and extensions it includes methods of determining or detecting the great majority of the substances met with in commercial soaps. The plan of procedure is so arranged as to permit of the examination of ordinary soaps being very simply conducted, while allowing any special ingredient to be sought for and determined.

#### A. DETERMINATION OF WATER.

The determination of the proportion of water in soap is important, and requires considerable care to ensure accurate results. If the soap be a solid one, a fairly representative sample should be reduced to fine shavings by scraping with a knife. A known weight is then exposed for some time to a temperature of 40° or 50° C., the heat being gradually raised to 100° C., and continued at that temperature as long as loss of weight is observed. The soap should not be allowed to melt.



A better method is to dissolve about 2 grm. of the soap in the minimum quantity of hot strong alcohol, and to pour the liquid on a known weight of clean dry sand, which is then exposed with frequent stirring to a temperature of  $110^{\circ}\text{C}$ . The traces of *alcohol* present in transparent toilet soaps which have been purified by solution in spirit, are volatilised with the water, and if 50 or 100 grm. of the sample be mixed with sand or powdered pumice, and gradually heated in a retort to  $120^{\circ}$ , the alcohol may be deduced from the specific gravity of the distillate. The water in soap may also be determined rapidly, and with ample accuracy for most purposes, in a manner recommended by Watson Smith (*Jour. Soc. Dyers and Colourists*, 1 31). From 5 to 10 grm. of the finely divided sample should be placed in a large porcelain crucible, set in a sand bath which is heated by a small Bunsen flame. The soap is continually stirred with a glass rod (weighed with the crucible) having a roughed and jagged end, a peculiarity which greatly facilitates the stirring and breaking up of the lumps of soap formed towards the end of the operation. The operation is usually complete in 20 to 30 minutes, and is known to be at an end when a piece of plate glass placed over the crucible (the flame being removed) is no longer bedewed with moisture. Care is required to prevent burning of the soap, but the odor thus developed is so characteristic that the manipulation is easily controlled. Smith finds the results trustworthy to 0.25 per cent.

The proportion of water in soap varies greatly. In the so-called "dry soaps," and in some of the best kinds of curd soap, it does not exceed 16 to 20 per cent, while in inferior soaps made from coconut oil it sometimes reaches 70 to 80 per cent.

#### B. SOLUTION IN PETROLEUM SPIRIT.

Under ordinary circumstances, the matter dissolved from dry soap on treatment with petroleum spirit consists merely of *unsaponified fats* or of *free fatty acids*. Insignificant proportions of unsaponifiable matter natural to fixed oils may also be present, and nitrobenzene and essential oils used for scenting the soap will also be dissolved. If Yorkshire grease has been used in manufacturing the soap, the residue may contain *cholesterol*, *Cetyl alcohol* from spermaceti and *myricyl alcohol* from beeswax and carnauba wax will also be present if these waxes have been employed. If added to the made soap, of course the unsaponified *waxes* will be dissolved out, instead of simply the solid alcohols resulting from their saponification. If the presence of *waxes* is suspected beforehand, or from the amount or appearance of the resi-

due obtained on evaporating a portion of the solution, the residual soap should be further exhausted with boiling toluene, which dissolves the wax-alcohols better than petroleum spirit

The residue from medicated soaps may also contain metallic *oleates* and free *carbolic* and *cresylic acids*, *thymol*, and *hydrocarbons*, such as vaseline and other neutral petroleum and tar products

When the nature or amount of the residue obtained on evaporating a small aliquot part of the petroleum spirit solution indicates the desirability of further examining it, the unevaporated portion should be treated in the manner directed in the following table —

#### SYSTEMATIC SEPARATION OF UNSAPONIFIED MATIERS FROM SOAP

Agitate the solution in petroleum spirit with dilute hydrochloric acid, and separate			
a Acid Solution. Examine for <i>heavy metals</i> (p. 9), <i>Pb</i> , <i>Hg</i> , <i>Cu</i> , <i>Zn</i> and <i>aluminum</i> , which, if found, must have existed in the soap as <i>salts</i> . Potassium and sodium <i>oleate</i> may also have been dissolved in the soap contained much <i>hydrocarbon</i> . If <i>metals</i> are found at this stage, the amount of fatty acids dissolved by petroleum spirit must be corrected to ascertain the fatty acids existing in the soap in a free state	b Petroleum Solution. Wash free from mineral acid by repeatedly agitating with small quantities of water. Add some alcohol and shake liquid with standard alkali and phenolphthalein for estimation of <i>fatty acids</i> (page 101). Separate and agitate petroleum spirit several times with small quantities of sodium hyposulphite solution, separating as before		
	c Petroleum Solution. Evaporate at a low temperature and observe odor, especially towards the end. Weigh residue and then determine <i>unsaponified fat</i> by Kautsky's process (page 51). In oleomarginal waxes, the <i>KHO</i> required divided by 0.19 gives the weight of glycerides, which, deducted from whole residue, gives that of the <i>hydrocarbons</i> , <i>alcohol</i> , &c. If desired, these may be isolated as on page 112, and further examined	d Alkaline Solution. Evaporate to small bulk, dilute with three measures of strong brine, and filter	e Precipitate consists of sodium salts of <i>fatty acids</i> existing in the soap either in the free state or as aluminum or other metallic <i>oleates</i>
			f Solution. Acidulate with dilute sulphuric acid, and separate layer of <i>phenols</i> , or filtrate portion of diluted solution with bromine, &c. (see page 281 and "Cresolate Oils," Vol. II, Pt. 2)

*Hydrocarbons*, such as petroleum, vaseline, and coal tar oils, are sometimes introduced into soap to a considerable extent. Although quite incapable of undergoing saponification, they may nevertheless exist in soap in notable proportion without their presence being suspected; for if not used in excessive amount, and especially if carnauba wax be also added, they remain in perfect solution when the soap is dissolved in water or alcohol, and, on decomposing the solution with an acid, they pass wholly into the oily layer of fatty and resin acids.

The presence of hydrocarbons in soap may sometimes be detected by the fluorescence exhibited by the ethereal solution of the fatty acids. If in considerable quantity, they may be partially separated

by subjecting the dry soap to a gradually increasing heat, when the hydrocarbons will distil, together with any other volatile matter which may be present.

The most satisfactory means of detecting and determining hydrocarbons in soap is to extract them by agitating the aqueous solution of the sample with ether and caustic alkali as described below. Any *unsaponified fat* will, however, be simultaneously dissolved by the ether, and must either be separated by saponifying the ether-residue with alcoholic potash, and again agitating the solution of the resultant soap with ether, or the original soap may be evaporated with alcoholic potash, and the residue dissolved in water and treated with ether.

The directions given in the foregoing table do not require further comment, except in the case of the method indicated for the determination of *phenols*. Carbolic and cresylic acids, and some other substances, are dissolved on treating the soap with petroleum spirit, and can be separated from the admixed fatty acids by precipitating the alkaline solution with brine, but the method is faulty for the following reason: soaps, and especially common household and soft soaps, are liable to contain free caustic alkali which will react with the coal-tar acids added to form bodies not dissolved by petroleum spirit, and hence the phenols obtained are only that portion not taken up by the free alkali present in the soap.

The assay of carbolic soap for the percentage of *phenols* and other *coal-tar products* is most conveniently and accurately effected by the following process, which has been extensively employed in the author's laboratory.—5 grm weight of the sample is dissolved in warm water with addition of from 20 to 30 c.c of a 10 per cent solution of sodium hydroxide, according to the proportion of phenols believed to be present. The cooled solution is then agitated with ether, and the ethereal layer separated and evaporated at a low temperature and weighed. The odor towards the end of the evaporation and that observed on heating the residue will give considerable information as to the nature of the admixture. Odors suggestive of gas-tar and burning gutta-percha are very common. The alkaline liquid separated from the ether is then treated in a capacious separator with excess of strong brine, which completely precipitates the fatty acids as sodium salts, while the phenols remain in solution. The liquid is well agitated to cause the soap to filter and is then passed through a filter. If the soap does not coagulate, an addition of a small quantity of tallow or palm-oil soap, previously dissolved in water, will usually determine separation. The precipitated soap is washed twice by agitating it with

strong brine, the washings being filtered and added to the main solution, which is then diluted to 1 litre. 100 c.c. of this solution ( $\approx 0.5$  gm. of the sample of soap) is then placed in a globular separator, and acidulated with dilute sulphuric acid, when it should remain perfectly clear.<sup>1</sup> Standard bromine-water is then added from a burette, the stopper of the separator inserted, and the contents shaken vigorously. More bromine-water is then added, and the agitation and addition repeated alternately until the liquid acquires a faint but permanent yellow tint, showing that a slight excess of bromine has been used. If crystallised phenol had been employed for making the soap, the addition of the bromine-water causes the precipitation of tribromophenol,  $C_6H_2Br_3O$ , in snow-white crystalline flocks, which allow the faintest yellow tint due to excess of bromine to be observed with great facility. If cresylic acid be the chief phenol present, the precipitate is milky and does not separate well from the liquid, but the end of the reaction can still be observed. The addition of a solution containing a known amount of crystallised phenol is a useful device in many cases, as the precipitate then curdles readily, and the yellow coloration can be easily seen.

The bromine solution is made by mixing in a separator one measure of saturated bromine-water with two measures of water. This solution is approximately 1 per cent., and should be run out from the tap of the separator into the Mohr's burette used for the titration. The burette should be closely covered, and the last few c.c. of the solution contained in it should never be employed for the titration, as it is apt to have become weak. The bromine-water must be standardised immediately before or after use, by a solution of Calvert's No. 2 or No. 5 carbolic acid, according to the kind of acid the titration has indicated to have been present in the soap. This solution is made by dissolving 0.5 gm. of the coal-tar acid in 20 c.c. of a 10 per cent. solution of sodium hydroxide, together with 5 gm. of a non-carbolic soap. The solution is then precipitated with brine in the same manner as the sample, the filtrate diluted to 1 litre, and 100 c.c. acidulated and titrated with the bromine used for the sample. The volume of bromine solution used is that required by 0.050 gm. of coal-tar acid of approximately the same quality as that contained in the soap.

The remaining portion of the liquid filtered from the precipitate of soap may be evaporated to a small bulk, acidulated with dilute sul-

<sup>1</sup> A precipitation at this stage indicates the incomplete removal of the fatty acids. In such case, 200 c.c. of the alkaline solution should be treated with common salt in powder, the solution filtered through a dry filter, and 100 c.c. of the filtrate acidified as before.

phuric acid, and the separated phenols measured, but the quantity is not sufficient to make the method satisfactory. It is generally better to employ the solution for the isolation of the bromo-derivatives. For this purpose it is acidulated with dilute sulphuric acid (without previous concentration), and bromine-water added in slight excess. From 5 to 10 c.c. of carbon disulphide are then added, the liquid well agitated, and the carbon disulphide tapped off into a small beaker. The aqueous liquid is agitated with fresh quantities of carbon disulphide (of 5 c.c. each) till it no longer acquires a red or yellow color. The carbon disulphide is then allowed to evaporate spontaneously, when a residue is obtained consisting of the brominated derivatives of the phenols present in the soap. If *crystallised carbolic acid* of fairly good quality had been introduced into the soap, the bromo-derivative is obtained in fine long needles having very little color, and, if all heating was avoided during the evaporation of the carbon disulphide, the weight of the residue multiplied by 0.281 gives a fair approximation to the amount of carbolic acid; but if a crude liquid article has been employed, consisting mainly of *cresylic acid* (e.g., Calvert's "No. 5 carbolic acid"), the bromo-derivative will be deep yellow, orange, or red, with little or no tendency to crystallise, and the weight will not afford even a rough indication of the amount of coal-tar acid present.

Lewkowitsch considers the following rapid process sufficiently accurate for practical purposes. Weigh off a somewhat large amount of the sample, say 100 grm., treat as described to separate the soap, boil down the solution of the phenate to a small bulk, transfer to a stoppered measuring cylinder of 50 or 100 c.c. capacity, add sufficient salt so that some remains undissolved, and acidify with sulphuric acid. The volume of the separated phenols is then read off and the number of cubic centimeters taken as so many grams.

The following table shows some of the results obtained in the author's laboratory by the assay of representative samples of commercial carbolic soap. The descriptions of the soaps given by the manufacturers are strictly adhered to, and in cases where two samples are described in the same words they were manufactured by different firms.—

DESCRIPTION OF SOAP	PHENOLS		RESIDUE	
	Per- centage	Nature	Per- centage	Odor on Heating
1 Medical carbolic soap, 20% pure,	55.5	Pure phenol		
2 Medical carbolic soap, 20% pure,	17.0	Pure phenol	4.2	Gutta-percha
3 Carbolic toilet soap, 10%,	4.6	Pure phenol	2.0	Crystalline
4 Carbolic toilet soap, 10%,	3.1	Pure phenol	1.0	Gutta-percha
5 Transparent carbolic soap,	3.2	Pure phenol		
6 Transparent carbolic soap,	1.5	Pure phenol		
7 Domestic carbolic soap,	4.8	Pure phenol		
8 Domestic carbolic soap,	6.1	Common carbolic		
9 No. 1 carbolic soap,	5.4	Common carbolic		
10 No. 2 carbolic soap,	3.8	Common carbolic		
11 Carbolic soap,	1.1	Common carbolic	1.0	
12 Carbolic soap,	0.5	Impure carbolic		
13 Carbolic soft soap, 10%,	3.9	Common carbolic		
14 Carbolic soft soap, 10%,	8.2	Common carbolic		
15 Carbolic soft soap,	0.16	Common carbolic		
16 De-infant soap,	none		4.6	Coal-tar oils
17 Sanitary soap,	0.75	Impure carbolic	1.6	Coal-tar oils

It will be observed that in No. 1 sample, described as containing 20 per cent. of crystallised carbolic acid, 30.5 per cent. was actually found, which result was confirmed by weighing the tribromophenol, which crystallised in beautiful colorless needles. In some cases the proportion of phenols found was notably less than the amount stated to be present, and this was especially the case with both No. 3 and No. 4, though these soaps were made by different firms. It must, however, be borne in mind that a loss of 2 or even of 3 per cent of phenol is liable to occur through evaporation.

#### C RESIDUE INSOLUBLE IN PETROLEUM SPIRIT

The portion of the sample not volatile at 100° and insoluble in petroleum spirit really constitutes the *soap proper*.

In analysing soap of known origin and general composition, it is often wholly unnecessary to go through the previous operations of drying and exhaustion with petroleum spirit. In such cases it is evidently preferable to weigh out 10 grm. of the original soap and at once treat it with hot water.

#### D AQUEOUS SOLUTION OF THE PURIFIED SOAP.

In most cases soap will dissolve almost completely in boiling water, but if a large quantity of the solvent be employed, hydrolysis occurs to a serious extent, and if such a liquid be filtered, a notable quantity of acid soap may be removed. Hence it is better when possible to separate any insoluble matter by decantation. When the proportion of insoluble matter is inconsiderable, there is no occasion to separate it,

as with proper management it will not interfere with the subsequent operations. An exception occurs in the case of calcium carbonate, which, if not removed, will neutralise acid and render the figure for the total alkali too high.

In many cases the aqueous solution of the soap may be advantageously agitated with ether at this stage. Such treatment obviates the necessity of previously extracting the dried soap with petroleum spirit, while it removes *hydrocarbons, unsaponified oil, and free fatty acids* in a very satisfactory manner. The ethereal layer having been separated (see page 52), the aqueous liquid is again shaken with ether, which is separated as before. The ethereal solution may then be treated in exactly the same manner as is directed for the petroleum spirit solution on page 280, while the aqueous liquid can be at once titrated with standard acid, though for convenience of subsequent manipulation of the fatty acids it is desirable first to remove the dissolved ether by boiling the solution in a capacious flask.

#### E. SEPARATION OF FATTY ACIDS.

For decomposing the aqueous solution of the soap, normal sulphuric acid possesses some advantages, and should be used in moderation, an excess of 5 to 10 c.c. beyond that necessary to combine with the alkali present being sufficient. Wright and Thompson prefer to substitute standard nitric acid, as it enables the sulphates to be determined by barium chloride in one portion of the filtrate, and the chlorides by silver nitrate in another.

The method of manipulation for the separation of the oily layer of fatty acids from the aqueous liquid depends on circumstances.

When the soap is chiefly a stearate or palmitate, as that made from tallow or palm oil, the liberated fatty acids are solid when cold, and in such cases there is no better plan than to effect their precipitation in a beaker or vessel, of such shape that the cake can be directly removed, wiped with blotting-paper, and weighed. Precipitation in a conical flask, as described on page 190, is advantageous in some cases.

If the fatty acids are liquid at the ordinary temperature, or form a cake deficient in consistency, a known weight of dry, bleached beeswax or stearic acid may be added to the hot liquid. The fatty acids become amalgamated with the melted wax, and, on cooling, a firm coherent cake is formed, which may be at once wiped and weighed. The weight of wax added (which should be about the same as that of the soap employed) being deducted from that of the cake, the weight of the crude fatty acids is at once found.

As a rule, the author prefers to affect the decomposition of the soap solution in a tapped separator, running off the aqueous liquid through a wet filter, and subsequently allowing the fatty acids also to run on to the filter, where they are washed with boiling water, and subsequently treated as described on page 51. This method of treatment is the best when it is desired to make a further examination of the separated fatty acids.

Coconut and palmnut oil soaps yield fatty acids not wholly insoluble in hot water. In such cases the precipitation of the acids should be conducted in a tolerably concentrated liquid, which may be advantageously saturated with common salt. The washing of the separated acids should be restricted, and bime may be advantageously used, while the drying should be effected with as little exposure to heat as possible.

#### F. SOLUTION SEPARATED FROM THE FATTY ACIDS

The method described in the table for determining the *total alkali* of soap is, in most cases, highly satisfactory. The result is not affected by the omission to treat the soap with petroleum spirit before dissolving it in water, and ordinary insoluble matters do not interfere. If, however, an insoluble carbonate be present, it will neutralise acid, and must be separated, or the figure for alkali will be too high (see p. 292).

Instead of at once adding an excess of standard acid, then titrating back, and thus ascertaining the volume required to neutralise the alkali of the soap, the standard sulphuric acid may be added gradually to the soap solution, until the neutral point, as indicated by methyl-orange, is reached. An excess of acid is then added, and the fatty acids separated as before.

The volumetric method of determining the alkali does not distinguish between potash and soda, and hence, if the nature of the alkali present be unknown, the determination is not absolute, but simply an expression of the alkali in terms of potash or soda. If further information be required, the examination must be made as described on page 293.

The solution separated from the fatty acids, and neutralised with standard alkali, will, of course, contain *alkali sulphates*. In addition, it may contain *sodium chloride, soluble fatty acids, glycerol, sugar, dextrin, starch, gelatin*, and other matters. For the detection and determination of these it is necessary to operate on separate aliquot portions of the solution.

If nitric acid has been used instead of sulphuric acid at the previous



stage of the process, the sulphates may be determined by precipitating an aliquot part of the solution with barium chloride.

a. *Sodium chloride* may be determined by titration with decinormal silver nitrate, or deduced from the weight of the silver chloride precipitate.

b. *Soluble fatty acids* rarely require determination in soap. If the precautions on page 285 are adopted in separating the fatty acids from coconut and palmnut oil soaps, only insignificant quantities of soluble fatty acids will remain in the aqueous liquid. If desired, these may be determined by distilling the acidulated solution, as described on page 49, but their amount may also be ascertained in the following simple manner. Titrate a certain volume of the solution with standard alkali, using phenolphthalein as an indicator. Titrate another portion of equal measure with the same alkali, using methyl-orange to indicate the point of neutrality. The alkali consumed in the second case corresponds to the free mineral acid only, while the difference between this and the first determination gives the volume of alkali required to neutralise the soluble acids present. One c. c. of normal alkali corresponds to 0.144 grm. of *caprylic acid*,  $C_8H_{16}O_2$ .<sup>1</sup>

J. A. Wilson (*Chem. News*, 1891, 205) employs the following process in the presence of soluble fatty acids —

1. The alkali in all forms is determined by titration with standard acid in the usual manner.

2. Another weighed quantity of the soap is decomposed in an Erlenmeyer flask with a slight excess of dilute sulphuric acid, and the flask kept on the water-bath until the fatty acids separate quite clear. The flask is placed in ice-water to cool and then filtered. The fatty acids are washed three times successively with 250 c. c. of boiling water, allowed to cool each time, and filtered. The united filtrates are diluted to a litre and 500 c. c. placed in a beaker and tinted with methyl-orange; decinormal alkali is then run in until the liquid acquires the

<sup>1</sup> A possible method of determining the total fatty acids in coconut and palmnut oil soaps is as follows — Separate the fatty acids in the ordinary manner, but in as concentrated a solution as possible. Agitate the aqueous liquid with a little ether, separate, and extract any dissolved fatty acids from the ether by agitating with dilute caustic soda solution. Employ the alkaline solution obtained to neutralise the main quantity of fatty acids, and add a few drops of phenolphthalein, and then more caustic soda solution, drop by drop, until the pink color just remains permanent. Then precipitate the hot liquid with a slight excess of magnesium sulphate, filter, wash with hot water, dry the precipitate at 100° C., and weigh. Ignite the precipitate and weigh the residual MgO. The difference is the weight of fatty anhydrides forming insoluble salts with magnesia. Evaporate the filtrate, dry the residue at 100° C., and weigh. Ignite and weigh again. The difference is the weight of fatty anhydrides forming soluble salts with magnesia.

usual color, after which a little phenolphthalein is added and the addition of standard alkali continued until a permanent pink is established. The amount used in the latter titration is due to soluble acids and is calculated to caprylic acid. The fatty acids in the flask and that on the filter are dried and weighed, and then dissolved in alcohol and titrated with half-normal alkali. The amount so used, together with that required for neutralisation of the soluble acids, deducted from the total alkali, gives the alkali existing in forms other than as soap.

Of course, if desired, the soap may be decomposed with standard sulphuric acid, methyl-orange added, and the alkali required for neutralisation noted; this, deducted from the total acid used, would give the acid equivalent to the alkali existing in all forms. In this manner are determined.—

Total alkali,	.	.	.	.
Combined alkali, . . . . .	.	.	.	.
Insoluble fatty acids,	.	.	.	.
Soluble fatty acids,	.	.	.	.

c. *Glycerol* may exist in soap in variable amount. In the absence of sugar, it may be determined with considerable accuracy by the permanganate process. When glycerol is present in considerable amount in soap, Lewkowitsch makes the determination by dissolving it in water, separating the fatty matter with acid, and filtering off. The filtrate is then neutralised with barium carbonate and boiled down to the consistency of syrup. The residue is then extracted with a mixture of three parts of 95 per cent. alcohol and one part ether, the alcoholic solution filtered and evaporated on the water-bath to small bulk, and finally dried under a desiccator. The glycerol in the residue may be determined by the acetin method. A more convenient method is that of Helmer with potassium dichromate (see under "Glycerol"). The presence of sugar renders the above methods wholly useless, and one of the plans described below must be adopted.

d. *Sugar* is rarely present except in transparent toilet soaps, but in these it sometimes exists to the extent of 20 to 30 per cent. of the entire weight, or in a proportion approaching that of the anhydrous soap present. Such soap is sometimes sold as "glycerin soap," though wholly destitute of glycerol.

According to Donath and Mayrhofer (*Zeit f. Anal. Chem.*, 1881, 383) the determination of sugar and glycerol may be made by adding to the solution slaked lime sufficient to combine with the sugar and an

equal quantity of washed and ignited sand, boiling down to the consistency of syrup, pulverising the cooled residue and exhausting it in a closed vessel with 80-100 c.c. of a mixture of equal parts of ether and alcohol. The glycerol will pass into solution, and, after cautious evaporation of the solvent, may be determined by the acatin or oxidation process. (See also "Isolation of Glycerol.")

Sugar may be determined by Fehling's solution, after inversion, without previously separating the glycerol, but the solution should be dilute and the boiling very limited in duration, or the glycerol will probably cause some reduction.

In an aqueous liquid containing no other bodies than sugar and glycerol, the amount of glycerol may be deduced from the specific gravity of the liquid. The sugar having been previously determined by Fehling's solution or other means, its effect on the specific gravity can be readily calculated, and this being deducted from the observed specific gravity, gives that due to the glycerol present in the liquid. (See "Glycerol") (See Addenda ")

*Organic matters*, such as starch, dextrin, gelatin, &c., may be detected by special tests, but their recognition is more easy and certain in residue L, left on treating the purified soap with alcohol.

#### G EXAMINATION OF THE OILY LAYER OF FATTY ACIDS.

The separation of the liberated fatty acids from the acidulated aqueous solution has already been described. If wax or stearic acid has been employed for the purpose of obtaining a solid cake, the further treatment of the fatty acids is practically limited to drying them and determining their weight. In many cases, however, it is of interest or importance to make a further examination of the oily layer, which in that case should be treated as described on page 113.

The oily layer may contain *fatty acids*, the acids of *resin* or *colophony*, *coal-tar products* which existed as salts in the original soap, and other bodies of acid character and limited solubility in water. If the treatment with petroleum spirit has been omitted, the oily layer may contain various *hydrocarbons*, *waxes* and *wax alcohols*, *unsaponified fat*, &c. In such a case the proximate analysis is best made as indicated in the table on page 280. When only fatty and resin acids are to be determined, they may be separated by Twitchell's method (p 107); but it must be remembered that any unsaponified oil may contaminate the resin acid and be determined as such. Resin acids may be detected by Liebermann's reaction, as follows.—A portion of the fatty acids is shaken up with acetic anhydride and heated gently. After

cooling, the acetic anhydride is drawn off by means of a pipette, and a drop of concentrated sulphuric acid added. In the presence of resin acids a fugitive violet color is produced. Morawski recommends the use of sulphuric acid of 1.53 specific gravity as less apt to produce interfering color. Coal-tar acids may be determined by the bromine-titration process described on page 281.

It is often important to ascertain the origin of the fatty acids from soap. In some cases this may be satisfactorily solved by a study of their physical and chemical properties. Thus, the melting and solidifying points of the fatty acids from various sources are given on pages 238 and 239, and Archbutt has communicated the following determinations of the specific gravities of the acids from various oils. The observations were made at the boiling point of water by means of a Sprengel-tube, and the figures express the specific gravities of the fatty acids at the boiling point of water, compared with water at 15.5° C.

FATTY ACIDS FROM	SPECIFIC GRAVITY	FATTY ACIDS FROM	SPECIFIC GRAVITY
Olive oil, genuine	8422	Nigroseed oil	8546
" " Gallipoli, )	8404	Linseed oil	8583
average )	8423	Trian oil	8580
Colza oil	8448	Lard oil	8438
Rape oil	8425	Tallow	8364
Cottonseed oil	8478	Palm oil	8367

Much information can be gained by determining the combining weight as described on page 236. The figures yielded by the acids from various oils are given on page 238, and in other cases they may be calculated from the saponification-equivalents recorded on page 55. The combining weight of the insoluble acids is usually less than the saponification-equivalent of the oil by about 13 to 14. This statement only applies to those oils yielding about 95 to 96 per cent. of insoluble fatty acids on saponification.

Similarly, the iodine-absorptions of the insoluble fatty acids (p. 237) are more or less characteristic of their origin, but are subject to the same limitations as are stated above to apply to the saponification-equivalents.

In cases in which the fatty acids are practically insoluble in water, a titration in alcoholic solution with standard alkali and phenolphthalein affords a simple and accurate means of ascertaining the proportion of *alkali existing in combination with the fatty and resin*

*acids*, as it is evident that the amount of alkali required for neutralisation of the separated acids must be the same as that with which they had been previously in combination.

The fact that the soaps produced by the saponification of *coconut* and *palmnut oils* are not readily precipitated by solution of common salt, may, according to W. Lant Carpenter, be employed for detecting the presence of these oils in soap. A sufficient quantity of the soap should be dissolved in hot water, and the fatty acids liberated by acidulating the solution, and separated without special washing or use of ether. Carpenter then directs 10 grm. of the fatty acids to be treated with 39 to 40 c.c. of a normal solution of caustic soda, or a volume just sufficient to dissolve them completely. The whole is then boiled, and the weight of the liquid brought to 50 grm. by evaporation or cautious addition of water. A saturated solution of common salt (previously boiled with a few drops of sodium carbonate and filtered from any precipitate) is then run in gradually from a burette, the liquid being constantly stirred and kept gently boiling. The addition is continued until the soap suddenly precipitates, a point which is usually sharply marked. The soap from ordinary oils is precipitated when from 8 to 10 c.c. of the salt solution has been added, but that from coconut oil requires an addition of more than 50 c.c. Mixtures of the fatty acids from coconut or palmnut oil with those from other oils will of course require a volume of brine intermediate between these two limits.

#### I. EXHAUSTION OF THE SOAP WITH ALCOHOL

If the original soap be tolerably dry, ordinary rectified spirit is usually sufficiently strong for the treatment at this stage; but if the sample contain much water, absolute, or nearly absolute, alcohol should be used, or the solution will have an objectionable tendency to gelatinise during filtration and other inconveniences will arise. It is recommended by both Leeds and Wright that the portion of the soap to be treated with alcohol should be a part of that previously exhausted with petroleum spirit, but, as pointed out by C. Hope, it is not possible to dry soap effectually without a notable conversion of the caustic alkali into carbonate. The treatment with alcohol can be effected either in the Soxhlet-tube, or by boiling the soap with the solvent, and filtering and washing in the usual way.

#### K. EXAMINATION OF THE ALCOHOLIC SOLUTION

a. The determination of the *free caustic alkali* existing in soap can.

be effected very simply and accurately by the method of C Hope described in the table, the error rarely exceeding 0.25 per cent of the total free alkali present. The test may be applied qualitatively, by dropping an alcoholic solution of phenolphthalein on to a freshly cut surface of the soap, when a red coloration will be produced, the intensity of which increases with the proportion of the alkali present. Caustic or carbonated alkali will also be indicated by the black or grey coloration produced by dropping mercurous nitrate on the freshly-cut surface. Each 1 c.c. of normal acid neutralised represents 0.0471 gram of  $K_2O$ , 0.0561 of  $KHO$ , 0.031 of  $Na_2O$ , or 0.040 of  $NaHO$ . Should it be desired to ascertain whether the free alkali consist of potash or of soda, the method described on page 294 must be employed.

It is possible to have a *negative* alkalinity shown at this stage. This result is due to, the presence of free fatty acid or a diacid salt, but acidity of the alcohol may produce the same effect. The volume of standard alkali required to be added before a pink color appears should be calculated to its equivalent of *oleic acid*, which is stated in the analysis as existing in the free state. Any difference between this amount and that found in the petroleum spirit solution is due to a partial neutralisation of the free acid coexisting in the imperfectly mixed soap. The following method of treating the alcoholic solution of a soap in such a manner as to allow of the determination of the leading constituents in a very rapid manner has been communicated to the author by C Hope—2 gram. of the soap are dissolved in hot absolute alcohol, a drop of phenolphthalein solution added, and carbon dioxide passed till any pink coloration is destroyed. The liquid is then filtered, the residue, consisting of *total impurities*, washed with hot alcohol, weighed, and then titrated with decinormal acid and methyl-orange to find the *alkali not existing as soap*. The alcoholic solution is evaporated to dryness at  $100^\circ$ , and the residue of *dry soap* weighed when constant. It is then ignited gently, treated with water, and the solution titrated with decinormal acid and methyl-orange to find the *alkali existing as soap*. The difference between this and the total residue before ignition gives the *fatty anhydrides*, which, multiplied by 1.03, gives the *fatty acids*. The *water* is found with sufficient accuracy by subtracting the sum of the weights of the impurities and dry soap from 100.00.

It is necessary to avoid confusion between the alkali existing in a soap in the form of caustic potash or soda, and that existing therein as a carbonate, silicate, or borate. If the determination be made in

the alcoholic solution, as recommended, the caustic alkali alone will be present, the other compounds capable of neutralising acid being insoluble in spirit. On the other hand, the standard acid required to neutralise the aqueous solution of the soap (page 286) includes that corresponding to any soluble *carbonate, silicate, and borate or aluminate* in the sample.

The alcoholic solution of the soap rendered neutral to phenolphthalein may be conveniently employed to determine the *alkali existing in combination with the fatty and resin acids* of the sample. To effect this, it is merely necessary to add a few drops of methyl-orange solution to the neutralised liquid, and then at once titrate with standard sulphuric or hydrochloric acid. The point of neutrality is sharply marked by the production of a pink color, and the accuracy of the results are all that could be desired.

In order to prevent misunderstanding, the volumetric methods of ascertaining the proportions of alkali existing in soap in various conditions may be recapitulated as follows —

*In alcoholic solution of soap* —1. Acid required to establish neutrality to phenolphthalein corresponds to *free caustic alkali*, and is calculated to  $\text{NaHO}$ ,  $\text{KHO}$ ,  $\text{Na}_2\text{O}$ , or  $\text{K}_2\text{O}$ , according to circumstances. 2. Acid subsequently required by same solution to produce neutrality to methyl-orange represents the *alkali existing as soaps of fatty and resin acids*.

*In residue insoluble in alcohol* —3. Acid required to produce neutrality to methyl-orange corresponds to *alkali existing as carbonate, silicate, and borate*.

*In aqueous solution of soap* —4. Acid required to produce neutrality to methyl orange corresponds to *total alkali*, whether existing as hydroxide, fatty acid soap, resin soap, carbonate, silicate, borate, aluminate, and soluble lime. This determination should therefore agree with the sum of 1, 2, and 3, or if any two of these have been determined the third will be the difference between their sum and the total alkali (4).

The volumetric determination of the alkali in soap gives no information as to whether it is potash or soda, or a mixture of them. To ascertain this it is necessary to separate them as sulphates or chlorides. This is best effected by treating the alcoholic solution of the soap which has been used for the determination of alkali, and is neutral to methyl-orange, with strong baryta-water, until the formation of a permanent pink tint shows that the liquid is distinctly alkaline to phenolphthalein. A saturated solution of barium chloride is then added, as

long as further precipitation occurs, when the liquid is filtered from the barium sulphate and barium soap. The filtrate is evaporated to dryness, and the residue cautiously ignited at the lowest possible temperature. The residue is dissolved in water, the solution filtered, and treated with ammonia and ammonium carbonate, the precipitate filtered off, the filtrate again evaporated to dryness, and the residue gently ignited and weighed. In the mixed *chlorides* thus obtained, the potassium and sodium may be indirectly deduced from the percentage of chlorine present, or the potassium may be directly determined as potassium platinum chloride in the usual manner. The determination of the chlorine by dissolving the residue in water, and carefully titrating one-half of the solution with decinormal silver nitrate, using neutral potassium chromate as an indicator, will usually give sufficient information, and will, at any rate, suffice to show whether the residue consists essentially of potassium chloride or of sodium chloride, or, if a mixture of the two, the approximate proportions in which they are mixed.

The following formula may be used for calculation:—

$$\text{Per cent of sodium chloride} = \frac{\text{Per cent of total chlorine} - 47.53}{0.1113}$$

#### L. RESIDUE INSOLUBLE IN ALCOHOL.

After drying and weighing the residue obtained at this stage, a minute quantity of it may be advantageously examined under the microscope, by which many substances will be revealed by their characteristic structure. Iodine solution will color starch granules blue and render them more distinct.

If starch be found under the microscope, it is sometimes desirable to treat the residue with cold water, and examine the solution thus obtained separately from that subsequently obtained by the use of boiling water. Starch and gelatin will be contained in the latter only, but sodium silicate may be present in both solutions, a circumstance which is apt to occasion an undesirable complication.

#### M. EXAMINATION OF THE AQUEOUS SOLUTION OF THE RESIDUE.

Before dividing the aqueous solution and titrating one-half with standard acid in the manner described in the table, it is sometimes desirable to make a direct determination of the carbon dioxide evolved on treatment with acid, so as to obtain a means of calculating the amount of *alkali carbonate* present. This is necessary when the soap contains borate or silicate in addition, but otherwise the car-



bonate can be deduced with accuracy from the titration of the solution with standard acid. To determine the carbonate directly, the concentrated solution should be treated with a moderate excess of standard acid in a carbon dioxide apparatus, and the evolved carbon dioxide ascertained by the loss of weight, precipitation as barium carbonate, or measurement in a nitrometer. 44 parts of  $\text{CO}_2$  correspond to 138.2 of  $\text{K}_2\text{CO}_3$ , or 106 of  $\text{Na}_2\text{CO}_3$ .

1 After expelling the last of the carbon dioxide by warming the acidulated liquid, the solution should be divided into two or more equal parts, in one of which the excess of acid is determined by titrating back with standard sodium carbonate and methyl orange, and hence the sum of the alkali existing in the four forms of *carbonate*, *silicate*, *borate*, and *aluminate* ascertained, while the other portion is examined for borate, silicate, and aluminate as in 2.

The solution which has been employed for the determination of the total alkali of the residue may then be divided into two or more equal parts, which may be employed for determining *sulphates* by precipitation with barium chloride, *starch* by the methods described in vol. 1 page 414, and to test for *gelatin* by means of tannin. If gelatin be found, it is best determined by treating another quantity of the soap with strong alcohol, and applying the Kjeldahl method to the residue. Gelatin contains about 17.9 per cent of nitrogen.

2. The other half of the aqueous solution of the residue insoluble in alcohol should be rendered distinctly acid with hydrochloric acid, and evaporated at  $100^\circ$  in porcelain. A slip of tumeric paper should be immersed in the liquid towards the end of the operation, and allowed to remain until the evaporation is complete. If a *borate* be present, the paper will become brownish red in color, and will be changed to green, blue, violet, or black on addition of caustic soda solution. The residue is treated with hydrochloric acid, water added, and the solution filtered. The residue of *silica* is washed, dried, ignited, and weighed. As the *sodium silicate* present in soap is not of constant composition, though usually approximately corresponding to the formula  $\text{Na}_2\text{Si}_2\text{O}_5$ , it is not possible to deduce the amount of alkali existing as silicate from the weight of the silica found; but, in the absence of borates, it may be ascertained by determining the carbon dioxide evolved on treating the aqueous solution of the residue insoluble in alcohol with dilute acid. This estimation will give the means of calculating the alkali existing as *carbonate*, and the remainder of the alkali of the residue must exist as *silicate* (or *aluminate*).

The filtrate from the silica may be conveniently employed for de-

termining *sulphates* by precipitation with barium chloride, or of *aluminium* by precipitation with ammonium hydroxide and of *calcium* in the filtrate by precipitation with ammonium oxalate. C Hope states that free lime is not unfrequently present in soap, and may be detected and determined at this stage. Its presence would tend to increase the "alkali" of the residue insoluble in alcohol.

#### N. RESIDUE INSOLUBLE IN PETROLEUM SPIRIT, ALCOHOL, AND WATER

After drying the residue at 100° and noting its weight, it is desirable to examine it under a low microscopic power, with a view of recognising characteristic organic structures, which can be seen much more distinctly after the removal of the soluble matters.

Whether any further examination of the residue is requisite necessarily depends on its amount and nature, and the object of the analysis. Among the various constituents of such a residue the following list comprises those most likely to be present:—

1. *Insoluble Organic Matters*, such as sawdust, bran, woody fibre from oatmeal.

2. *Mineral Pigments and Coloring Matters*, as red ochre, burnt umber, various other ferruginous materials, red lead, vermilion, Scheele's green, chrome green, ultramarine.

3. *Mineral Matters used as Scumers*; such as sand, powdered quartz, pumice, and infusorial earth.

4. *Mineral Matters used as Adulterants or "Fillings"*; such as china clay, steatite, barium sulphate, chalk, and whiting.

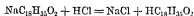
The systematic recognition and determination of these and other possible additions belong to inorganic analysis. It is sufficient here to indicate the following simple method of classification, with a view to facilitate further examination.

*Organic matters* may be approximately determined by igniting an aliquot portion of the residue. The loss will include the volatile constituents of china clay, whiting, red ochre, &c., as well as any vermilion which may be present.

By treatment with dilute hydrochloric acid, the original or ignited residue may be divided into *soluble* and *insoluble constituents*. The former include whiting, chalk, ultramarine, Scheele's green, oxide of iron, and the greater part of the ferruginous pigments, while barium sulphate, steatite, sand, quartz, pumice, kieselguhr, china clay, chrome green, and vermilion are but little acted on.

### Interpretation of the Results of Analysis of Soaps.

An ordinary "soap" may be regarded as the hydrated salt of a higher fatty acid, or a mixture of such salts. When a soap is decomposed by a dilute mineral acid, as occurs in the course of an analysis, free fatty acids are produced, together with a chloride or other salt of the alkali-metal. Thus, in the case of sodium stearate, which is a typical soap, the reaction is as follows —



Calculating from this formula, it is found that, on decomposition with acid, sodium stearate yields 92.8 per cent. of stearic acid. Similarly, the alkali in the soap would be stated to be 10.13 per cent., so that the analysis would be—

Stearic acid,	. . .	92.81 per cent
Soda ( $\text{Na}_2\text{O}$ ),	. . .	10.13 " "
		<hr/> 102.94 " "

This statement shows an excess of nearly three per cent., owing to the hydrolysis which takes place in decomposition. It is evident that if the basic constituent of a soap be stated as anhydrous alkali, a correction must be made in the actual weight of fatty acid found to bring it to the corresponding quantity of anhydride<sup>1</sup>. 568 parts of stearic acid,  $\text{C}_{18}\text{H}_{35}\text{O}_2$ , correspond to 550 of stearic anhydride,  $\text{C}_{36}\text{H}_{70}\text{O}_3$ , and the proportions of the respective anhydrides corresponding to palmitic and oleic acids are not very different from the above. Hence in soaps made from palm oil, olive oil, and tallow, the necessary cor-

<sup>1</sup> In a complete analysis of a soda soap, the constituents should be stated in the following manner —

	PER CENT	PER CENT
* Fatty anhydrides,	—	—
† Soda existing as soap,	—	—
Silica,	—	—
† Soda existing as silicate,	—	—
† Sodium carbonate,	—	—
† Sodium hydroxide (caustic soda, $\text{NaHO}$ ),	—	—
Sodium sulphate,	—	—
Sodium chloride,	—	—
Lime,	—	—
Iron oxide,	—	—
Water,	—	—

\* = Fatty acids—per cent

† = Total detergent alkali, as  $\text{Na}_2\text{O}$ —per cent

DESCRIPTION OF SOAP	ORIGIN	FATTY AND RESIN ANALYSES	SODA EXTRACT AS SOAP	SILICA	SODA EXTRACT AS SOAP	SODIUM CARBONATE HYDRATE	SODIUM CHLORIDE	SODIUM SULPHATE	Loss, H <sub>2</sub> O	WATER TOTAL	FATTY AND RESIN ACIDS
1 "White," No. 1	Tallow	69.06	8.98	0.01	None	27	49	16	07	21.11	100.15
2 " " No. 2	{ Tallow and coconut oil	60.50	6.82	0.06	None	06	11	12	16	32.20	100.03
3 " " No. 3	Do	55.71	6.90	0.03	None	92	18	Trace	08	36.54	100.36
4 " " No. 4	Do	44.21	6.23	7.02	2.46	75	32	34	04	38.14	99.77
5 "Cold Water," No. 1	{ Tallow, rosin, and cottonseed oil	71.30	7.93	1.07	0.48	75	56	50	16	17.41	99.84
6 " " No. 2	Do	49.25	7.00	2.34	1.01	75	51	00	30	38.18	99.82
7 "Olive Oil," No. 1	Olive oil	71.20	7.58	0.06	0.03	22	66	17	20	19.70	99.82
8 "Muscovite," No. 1	Chiefly olive oil	62.63	7.27	0.06	0.01	77	76	00	16	28.20	100.21
9 "Palm Oil," No. 1	Palm oil	59.28	6.65	0.42	0.01	59	47	13	16	2.35	99.86
10 "Mottled," No. 1	Palm oil	58.89	5.76	6.40	1.29	102	178	72	05	38.70	97.19
11 "Satin," No. 1	Tallow and rosin	59.42	6.76	0.02	None	92	41	Trace	05	11.20	99.15
12 "Glycerine," No. 1	Do	42.11	4.14	5.64	1.50	27	7	Trace	14	12.88	99.61
13 "Palm Roast," No. 1	Do	60.90	7.22	0.04	None	10	46	12	02	31.22	100.03
14 " " No. 2	Do	45.20	5.00	0.42	0.18	15	65	10	10	43.00	99.80
15 " " No. 3	Do	79.92	4.70	0.02	0.25	29	148	18	15	52.40	99.09
16 "Milling," No. 1	Do	63.06	7.25	0.02	None	10	165	15	30	27.47	100.00
17 "Yellow," (for foreign markets) No. 1	Do	10.90	1.36	0.03	None	Trace	257	56	14	84.00	99.56
18 "Maize," for emigrants	Palm oil	19.42	3.11	9.00	3.98	300	513	55	16	53.32	97.17

reaction of the observed weight of fatty acids to the corresponding quantity of fatty anhydrides may be made by multiplying by the factor 97, 100 parts of  $C_{18}H_{35}O_2$  representing approximately 97 of  $C_{18}H_{17}O_2$ . But in the case of coconut and castor-oil soaps, and many others made with mixed oils, this factor is far from accurate, and hence it is in all cases decidedly preferable to determine the mean combining weight of the isolated fatty and resin acids, as described on page 236, and calculate the corresponding weight of fatty anhydride therefrom. The mean combining weight of the anhydride is always 9 less than that of the corresponding acid. The usual figures for the fatty acids isolated from various fatty oils are given on page 238.

Gassler (*J. S. C. I.*, 1882, 370) gives the following analyses of German resin soaps in comparison with Sinclair's "cold water soap" —

DESCRIPTION OF SOAP	FATTY ACIDS	RESIN	SODA	TALC	WATER
German soap, (German soap)	56.25	14.75	12.75		16.25
Sinclair's soap, . . .	51.65	17.15	12.55		16.45
	46.57	23.13	12.00	1.00	18.00

A considerable number of analyses of soaps have been published, but there are comparatively few on which much reliance can be placed. In the great majority of cases the observers appear to have been content to state the amount of fatty acids and alkali as deduced from the ash, the remainder being entered as "water, &c." Such meagre and inexact information as is supplied by such "determinations" is of very little value. The author is indebted to Mr. C. Hope for the valuable analytical data contained in the table on page 298. Samples 10 and 18 were prepared by the "cold process," and hence contained the glycerol produced by the saponification. This accounts for the sum of the estimated constituents being sensibly below 100.00. Samples 3, 4, and 12 were the only three which contained free caustic alkali, and in these it only reached the proportions of 0.16, 0.26, and 0.15 per cent of  $NaHO$  respectively. Hope points out that a striking feature of the analyses is the variable composition of the silicate existing in the soap, although as added it is tolerably constant in composition. This is attributed by Hope to the property possessed both by rosin and fats of taking alkali from sodium silicate, in which case the change will occur only in those soaps to which the silicate was added before saponification was complete.

W. Lant Carpenter gives the following analyses in his treatise on *Soaps and Candles* —

DESCRIPTION OF SOAP	FATTY ACIDS	SODA AS SOAP	SODA IN OTHER FORMS	SILICA	NEUTRAL SALTS	WATER	TOTAL
Prunrose soap as in South and West of England,	62.3	6.7			0.2	32.8	102.0
Prunrose soap as in North of England,	42.66	5.11	1.21	0.91	0.55	50.40	101.17
Genuine "cold water" soap,	70.2	7.3	1.8	1.6	0.4	22.0	103.3
Manufacturers' neutral curd soap,	67.9	7.0	0.0		0.2	28.0	103.1
Manufacturers' brown oil soap, from oleic acid,	68.60	7.88	1.00		1.00	21.00	99.48

M Dechan (*Pharm. Jour* [3], xv. 870) gives the following as the average composition of a number of samples of the chief soaps of pharmacy examined by him —

DESCRIPTION OF SOAP	FATTY ACIDS	COMBINED ALKALI	FREE ALKALI	SILICA	SULPHATES AND CHLORIDES	INSOLUBLE MATTER	WATER	INSOLUBLE IN ALCOHOL
Hard soap ( <i>Sapo durus</i> ),	81.5	9.92	08	00	28	0.2	10.65	0.5
White Castile soap ( <i>Sapo castil. alb.</i> )	76.7	9.14	00	00	36	0.9	13.25	0.6
Mottled Castile soap,	68.1	8.9	19	15	64	0.8	21.70	1.3
Tallow soap ( <i>Sapo animalis</i> ),	78.3	9.57	28	60	47	0.4	12.50	1.1
Soft soap ( <i>Sapo molli</i> ),	48.5	12.6	.8	17	93	1.0	39.50	1.6

Partial analyses of various representative samples of carbolic soap are given on page 284

But few complete analyses of soft soap have been published, but the proportion of water in samples of good quality is usually between 35 and 45 per cent, whilst the anhydrous oxide ( $K_2O$ ) varies from 8.8 to 11.2 per cent

In forming an opinion as to the quality of a soap, the application to be made of it is a primary consideration. In practice, water in moderate proportion must be regarded as a useless but unavoidable constituent, but if present in the enormous proportion sometimes observed it can only be regarded as an adulterant.

In some of the best brands of opaque toilet-soap made by special methods, the proportion of water does not exceed 10 or 12 per cent, but the majority of the best qualities of soap, known as Marseilles,

curd, brown Windsor, honey, and pruneose, contain from 17 to 24 per cent. of water. In some of the transparent toilet soaps, made by solution in alcohol, the proportion of water is very small (9 to 10 per cent.), but this advantage is more than counterbalanced by the presence of 20 to 30 per cent of sugar. Transparent soaps made in other ways, as by the "cold process," rarely contain half their weight of actual soap, the remainder consisting of water and sugar.

Practically, the proportion of *alkali* in a soap is the best single test of its quality, but here again a distinction must be drawn between alkali existing in combination with fatty and resin acids, or, in other words, as true soap, and that existing in other conditions, particularly the caustic state. Wright arranges toilet soaps in three classes, according to the proportion the "free" or *inorganic alkali* bears to the *alkali existing as soap*. Thus, soaps containing less than 25 parts of free alkali for 100 of alkali as soap are arranged in the first class, those containing between 25 and 75 in the second, and those containing more than 75 in the third class. But, in judging of the quality of a toilet soap, Wright also takes into account the freedom of the soap from adulterants, "filling," water, and "closing up" agents, and from poisonous coloring matters, as also the nature and quality of the fatty matters used as basis, and their freedom from rancidity.

Although the absence of a notable proportion of "free" alkali is important in the case of toilet soaps, owing to its powerful action on the skin, it does not follow that a similar absence of alkali is advantageous under other conditions. On the contrary, for scouring and household purposes, a limited proportion of free alkali is advantageous, and in the case of some soaps used by manufacturers the presence of a very considerable proportion of *caustic alkali* is essential to success, a solution of alkali with sufficient soap in it to cause lathering being preferred. A neutral soap, however pure, will for such uses be regarded as deficient in "strength," and will often cause trouble through the precipitation of free fatty acid or acid soap in the fabric with which the soap is used.

The nature and origin of the acids are sometimes of interest in judging of the suitability of a soap for certain purposes. The presence of resin acids, and of the acids from coconut or palmnut oil can be ascertained as described on page 289 *et seq.*, and it is rarely of interest to inquire further, except in the case of soap containing coal-tar acids, which can be examined as described on page 281.

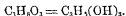
The legitimate character of the various additions to soap must be judged of on the merits of each case, but, as a general rule, the less

extraneous matters present the better. It is said that, for some purposes, as in the treatment of wool and silk, a small proportion of starch is an advantage. In contracting to supply manufacturers of textile fabrics, the soapmaker is frequently obliged to settle definitely the proportions of fatty acids, resin, alkali, and potato-starch which shall be present in the soap. A soap suitable for fulling cloth and for other purposes should not contain less than 40 per cent of fatty acids, nor more than 5 per cent of resin and 6 of potato-starch.

Dextrin, sugar, starch, Irish moss, and gelatin are in most cases purely adulterants, as also are kaolin, barytes, and other insoluble earthy matters; but soluble carbonates, silicates, and borates have marked detergent properties.

## GLYCEROL GLYCERIN

Tritenyl Alcohol.



Glycerol is a triatomic alcohol, and bears the same relation to ethyl alcohol that orthophosphoric acid bears to nitric acid. The name glycerol has reference to its chemical position as an alcohol. It is a constant product of the ordinary fermentation of sugar, and hence is a natural constituent of wine, beer, and other fermented liquids. It is produced by the saponification of the fixed oils, and the commercial article is always obtained by this means (see pages 44-47). The term "glycerin" is conveniently reserved as a designation of commercial forms consisting of true glycerol with variable amounts of impurities. Pure glycerol is a colorless, viscid liquid, without odor, but having an intensely sweet taste. It is optically inactive.

The specific gravity of absolute glycerol has been determined by a number of observers, whose results are not in entire agreement. The following are the specific gravities given by the authors in question, for the temperatures at which their observations were made, together with the corresponding figures for a uniform temperature of 15° C. The latter have, when necessary, been calculated by the author, taking Gerlach's value of 0.00065 as the decrease in the specific gravity of glycerol for a rise of temperature from 15° to 16° C. The glycerol employed by Lenz (*Zeits. Anal. Chem.*, 1880, 297) had its composition calculated from the results of an elementary analysis, Strohmeyer (*Monatsh. für Chemie*, v. 61) employed crystals of glycerol from which adhering liquid had been removed by pressure, while



Gerlach (*Die Chemische Industrie*, vii. 281) used glycerol which had been heated till it boiled constantly at 290° C.

OBSERVER.	OBSERVED SPECIFIC GRAVITY (Water at same temperature = 1)				CALCULATED SPECIFIC GRAVITY (Water = 1)
	At 12°	At 15°	At 17.5°	At 20°	At 15° C
Champion and Pellet . .		1.2640			1.2640
Fabry . . . . .			1.261		1.2626
Fuchs . . . . .		1.266			1.2660
G. T. Gerlach . . . .		1.2653		1.2620	1.2651
F. Hoffmann . . . .			1.267		1.2686
W. Lenz . . . . .	1.2691				1.2672
Skalweit . . . . .		1.2650			1.2650
Stohmer . . . . .			1.262		1.2620
Vogel . . . . .		1.266			1.2660
Mean . . . . .					1.2651

Chevreul and Schweikert give the specific gravity of glycerol as 1.267, but do not state the temperature of the determination. Sulman and Berry (*Analyst*, xi. 12) prefer the higher determinations, adopting the value 1.2675. The number 1.2665 may be regarded as being, on the whole, a preferable value for the specific gravity of absolute glycerol at 15° C.

At -40° glycerol solidifies to a gum-like mass. When kept for a long time at 0° rhombic crystals are formed, their production being greatly facilitated by the presence of a ready-formed crystal. The crystals are hard and gummy, but deliquescent.

Glycerol boils under the ordinary pressure at 290° C, according to some observers with slight decomposition. A small proportion of water greatly lowers the boiling point, a specimen containing 5 per cent of water boiling at 164° C. On the other hand, G. T. Gerlach recommends the constant boiling point of glycerol as a convenient means of determining the 290° point on high-temperature thermometers. Under diminished pressure it distils without change. The boiling point is 179.5° C for a pressure of 12.5 mm, and 210° C. for a pressure of 50 mm. It is not volatile at the ordinary temperature, but evaporates to an appreciable extent at 100°. Contrary to the statements of Nessler and Barth, Hohner has shown (*Analyst*, 1887, 67) that glycerol is not volatilised with aqueous vapor from dilute solutions. When evaporated at the boiling temperature appreciable loss does not occur until the solu-

tion contains about 70 per cent. It is highly hygroscopic, absorbing as much as half its weight of water when exposed to damp air. It is miscible with water in all proportions, the specific gravity of the mixture decreasing tolerably regularly with the proportion of glycerol, as shown in tables given below.

Glycerol is neutral in reaction, and acts as an antiseptic, even when largely diluted, but by schizomycetic fermentation it yields butyric and propylonic alcohols. It is miscible in all proportions with alcohol, but is insoluble in chloroform, benzene, petroleum spirit, carbon disulphide, or fixed oils, and nearly insoluble in ether, from which it separates any alcohol or water. It is soluble in a mixture of two volumes of absolute alcohol and one volume of ether,—a fact which may be employed to separate it from the sugars, gums, gelatin, and various salts. Another useful solvent is a mixture of equal weights of chloroform and alcohol, in which liquid the sugars, dextrin, gums, and many extractives are insoluble.

Glycerol possesses remarkable solvent properties, dissolving many bodies with greater facility than does water. This is true of iodine, phenol, mercuric iodide, and the alkaloids. Even silver chloride is very sensibly soluble in glycerol. Glycerol also dissolves the caustic alkalis, potassium sulphate and chloride, the corresponding sodium and copper salts, the vegetable acids, and all deliquescent salts. It removes ferric chloride and thiocyanate, auric chloride, and some other substances from ethereal solution on agitation with them.

The precipitation of chromic solutions by ammonium hydroxide and of cupric solutions by fixed alkalis is wholly or partially prevented by the presence of glycerol. With the alkaline earths and lead oxide glycerol yields compounds which are soluble in water, and the solutions of which are not decomposed by carbonic acid.

When gently heated with solid caustic potash, glycerol is converted into potassium acetate and formate, with evolution of hydrogen. When heated with a dehydrating agent (*e.g.*, concentrated sulphuric acid) irritating fumes of acrolein (acrylic aldehyde),  $C_3H_3COH$ , are evolved, smelling like burning fat. Glycerol is very readily oxidised to carbon dioxide and water, but when carefully treated with nitric acid it is converted into a mixture of oxidation-products in which oxalic acid, glyceric acid ( $C_3H_5O_4$ ), and other organic acids occur. By treatment in dilute aqueous solution with potassium permanganate, in presence of excess of caustic alkali, glycerol is oxidised in a very definite manner with formation of oxalic and carbonic acids. By treatment with potassium dichromate and sulphuric acid, it is com-

pletely oxidised to carbon dioxide and water. These reactions are utilised for the determination of glycerol (see page 314 *et seq.*).

### GLYCEROL ESTERS

By treatment with a cold mixture of fuming nitric and concentrated sulphuric acid, glycerol is converted into tritenyl nitrate or "nitro-glycerin,"  $C_3H_5(O NO_2)_3$ .

On mixing glycerol with strong sulphuric acid, a body of the formula  $C_3H_5(OH)_2SO_3H$  is produced, which has acid properties and forms soluble but unstable barium, calcium, and lead salts.

Glycerol-phosphoric acid,  $C_3H_5(OH)_2PO_4H_2$ , is obtained by the action of metaphosphoric acid or phosphoric anhydride on glycerol. It is of interest as being a proximate product of the decomposition of the highly complex phosphorised constituents of the brain. The calcium salt,  $CaC_3H_5(OH)_2PO_4$ , is easily soluble in cold water, but separates, on warming the solution, in snow-white glistening tablets or scales, which redissolve on cooling.

Glycerol dissolves large quantities of arsenious oxide to form a compound of the formula  $C_3H_5AsO_3$ , tritenyl arsenite, which has been employed by calico-printers for fixing aniline colors. It is an amber-yellow, fatty substance, melting at  $50^\circ$  to a thick liquid which is soluble in glycerol and in water, but is decomposed by excess of the latter liquid.

When 3 parts of glycerol are heated to about  $160^\circ C$  with 2 of boric acid, tritenyl borate,  $C_3H_5BO_3$ , is formed, which has been patented as a preservative agent under the name of "boroglyceride."

By heating glycerol with organic acids, esters are formed, of a composition dependent on the conditions of their formation. These esters are often called glycerides and are specifically designated by names ending in *in*, the mono-, di-, and tri acetates being called respectively monacetin, diacetin, and acetin. Similarly, stearic acid gives rise to stearins, oleic acid to oleins, butyric acid to butyrins, and so forth. The stearins, palmitins, and oleins have already been described.

### Detection of Glycerol.

When in a state of reasonable purity and concentration, glycerol may be recognised by its physical properties, no other substance likely to be met with exhibiting the combined characters of a dense viscous liquid of sweet taste and neutral reaction, miscible with water and alcohol in all proportions; volatile at a high temperature,

burning with a blue flame when kindled, and leaving no carbonaceous residue

The most characteristic reaction of glycerol is its behavior when heated in a concentrated state with potassium hydrogen sulphate, whereby it is converted into acrolein,  $C_3H_4O$ , with elimination of the elements of water. The acrolein is recognisable by its extremely penetrating odor, resembling that of burning fat, and its property of causing a flow of tears. If the vapors be passed into water, the warm solution will be found to have the property of reducing ammonio-silver nitrate, with formation of a mirror of metallic silver.

If two drops of concentrated glycerol be treated in a dry test-tube with two drops of fused carbolic acid and the same quantity of strong sulphuric acid, and the mixture heated very cautiously over a flame to about  $120^{\circ} C$ , a brownish yellow mass will be produced, which, after cooling, dissolves in water, to which a few drops of ammonium hydroxide have been added, with splendid carmine-red coloration.

According to Reichl minute quantities of glycerol can also be detected by boiling the solution to be examined with a minute quantity of pyrogallol and a few drops of sulphuric acid diluted with an equal volume of water, when a red color will be produced, changing to violet-red on adding stannic chloride. Carbohydrates and various alcohols give similar reactions.

In common with other polyhydric alcohols glycerol acts on borax to form a compound having an acid reaction to litmus, whereas the original aqueous solution of borax has an alkaline reaction. In the case of glycerol, tritenyl borate,  $C_3H_5BO_3$ , is formed, together with sodium metaborate,  $NaBO_2$ . The reaction may be utilised both in the wet and the dry way. Semier and Lowe recommend that the solution to be examined should be made faintly alkaline to litmus with dilute solution of soda, and a bead of borax (made by fusing the salt on a loop of platinum wire) dipped into it. The bead is allowed to rest for a few minutes, so as to allow solution to take place on its surface, and is then held in the flame of a Bunsen burner. A more delicate plan is to place some powdered borax in a watch-glass, pour on it some of the faintly alkaline liquid to be tested, and, by means of a looped platinum wire, introduce some of the mixture into the flame. In either case a deep green flame will be produced if a moderate quantity of glycerol be present, but the reaction becomes indistinct if the liquid contains less than 5 per cent. For detecting glycerol in beer, wine, milk, &c., 50 or 100 cc of the liquid should be evaporated to dryness on the water-bath, the residue extracted with absolute alcohol, the solution

so obtained again evaporated, and the resultant residue moistened with a few drops of water and tested with borax as above described. Ammonium salts, glycol, and erythrol give a similar reaction to glycerol. Ammonium salts may be thoroughly removed by evaporating the original liquid with sodium carbonate.

The reaction of glycerol with borax has been very thoroughly studied by W. R. Dunstan, who recommends the following mode of procedure.—To 2 c c of a dilute solution of borax in water (1 part in 200) sufficient of an alcoholic solution of phenolphthalein is added to color the liquid rose red. The liquid to be tested for glycerol is rendered neutral or very faintly alkaline to litmus, and gradually added to the borax solution until the rose color is discharged. The liquid is then heated to boiling, when the red color will be restored, to disappear again on cooling the solution. Excess of glycerol is to be avoided, otherwise the alkalinity of the solution, to which the pink coloration is due, is only partially restored by boiling. Using 2 c c of the borax solution, about 5 c c of a 2 per cent solution of glycerol must be added to destroy the color, and the limit of reaction is practically reached with a solution of this strength. The reaction is also given by mannitol, erythrol, dextrose, levulose, lactose, and mycose, but not by sucrose, guanicol, pyrogallol, and saligenol also give the reaction. Orcinol and resorcinol, when added in large quantity, partially destroy the red color, but it is not restored by boiling. The reaction is a more delicate one for mannitol than for glycerol, and the influence of dilution is not so great. Ammonium salts discharge the red color, but it is not restored on heating.

#### Determination of Glycerol.

The accurate determination of glycerol, when existing in a complex mixture together with other neutral organic and inorganic matters, cannot be said to have received a satisfactory solution under all circumstances. The problem is further complicated by the fact that solutions of glycerol cannot be highly concentrated without serious loss from volatilisation, and that the presence of glycerol materially increases the solubility of many substances in aqueous and alcoholic solutions.

Gerlach has described a method and apparatus for deducing the percentage of glycerol in aqueous solution, from an observation of the vapor tension.

F. Strohmayer proposed to estimate glycerol in admixture with water by observing the refractive index of the liquid, which can be readily

and accurately effected by means of the refractometer. The method might be useful when the volume of glycerol is not sufficient to permit a determination of its specific gravity.

When occurring in admixture with water only, the proportion of glycerol present can be deduced with a very fair approach to accuracy from the specific gravity of the liquid. Tables of specific gravities of mixtures of glycerol with water have been published by several chemists.

The following table, by Skälweit (*Repositor. d. analyt. Chemie*, v 18), gives the specific gravities and refractive indices for the sodium ray, at 15° C., of mixtures of glycerol and water in various proportions —

PER- CENT- AGE OF GLY- CEROL	SPECIFIC GRAVITY AT 15° C.	REFRACT- IVE INDEX AT 15° C.	PER- CENT- AGE OF GLY- CEROL	SPECIFIC GRAVITY AT 15° C.	REFRACT- IVE INDEX AT 15° C.	PER- CENT- AGE OF GLY- CEROL	SPECIFIC GRAVITY AT 15° C.	REFRACT- IVE INDEX AT 15° C.
0	1.0000	1.3310	14	1.0558	1.3771	68	1.1799	1.4265
1	1.0024	1.3312	15	1.0585	1.3785	69	1.1827	1.4280
2	1.0048	1.3314	16	1.0612	1.3799	70	1.1855	1.4295
3	1.0072	1.3316	17	1.0639	1.3813	71	1.1882	1.4310
4	1.0096	1.3318	18	1.0666	1.3827	72	1.1909	1.4324
5	1.0120	1.3320	19	1.0693	1.3840	73	1.1936	1.4339
6	1.0144	1.3322	20	1.0720	1.3854	74	1.1964	1.4354
7	1.0168	1.3324	21	1.0747	1.3868	75	1.1990	1.4369
8	1.0192	1.3326	22	1.0774	1.3882	76	1.2017	1.4384
9	1.0216	1.3328	23	1.0801	1.3896	77	1.2044	1.4399
10	1.0240	1.3330	24	1.0828	1.3910	78	1.2071	1.4414
11	1.0264	1.3332	25	1.0855	1.3924	79	1.2098	1.4429
12	1.0288	1.3334	26	1.0882	1.3938	80	1.2125	1.4444
13	1.0312	1.3336	27	1.0909	1.3952	81	1.2152	1.4459
14	1.0336	1.3338	28	1.0936	1.3966	82	1.2179	1.4474
15	1.0360	1.3340	29	1.0963	1.3980	83	1.2206	1.4489
16	1.0384	1.3342	30	1.0990	1.3994	84	1.2233	1.4504
17	1.0408	1.3344	31	1.1017	1.4008	85	1.2260	1.4519
18	1.0432	1.3346	32	1.1044	1.4022	86	1.2287	1.4534
19	1.0456	1.3348	33	1.1071	1.4036	87	1.2314	1.4549
20	1.0480	1.3350	34	1.1098	1.4050	88	1.2341	1.4564
21	1.0504	1.3352	35	1.1125	1.4064	89	1.2368	1.4579
22	1.0528	1.3354	36	1.1152	1.4078	90	1.2395	1.4594
23	1.0552	1.3356	37	1.1179	1.4092	91	1.2422	1.4609
24	1.0576	1.3358	38	1.1206	1.4106	92	1.2449	1.4624
25	1.0600	1.3360	39	1.1233	1.4120	93	1.2476	1.4639
26	1.0624	1.3362	40	1.1260	1.4134	94	1.2503	1.4654
27	1.0648	1.3364	41	1.1287	1.4148	95	1.2530	1.4669
28	1.0672	1.3366	42	1.1314	1.4162	96	1.2557	1.4684
29	1.0696	1.3368	43	1.1341	1.4176	97	1.2584	1.4699
30	1.0720	1.3370	44	1.1368	1.4190	98	1.2611	1.4714
31	1.0744	1.3372	45	1.1395	1.4204	99	1.2638	1.4729
32	1.0768	1.3374	46	1.1422	1.4218	100	1.2665	1.4744
33	1.0792	1.3376	47	1.1449	1.4232			

The specific gravity of glycerol is best observed by means of the hydrostatic balance, as the indications furnished by the hydrometer are liable to be two or three degrees (.002 or .003) in excess of the true amount.

In pouring the glycerol, great care should be taken that no bubbles

of air are formed, which in the cold may require a very long time to rise to the surface. The liquid should be poured so that it flows down the side of the cylinder.

Hehner (*J S C I*, 1889, 8) prefers the use of a Sprengel tube, which is filled, by means of an air-pump, with the glycerol, previously heated in a closed flask on the water-bath to reduce the viscosity. The tube is then immersed in water at 15.5°. Should the temperature be not exactly 15.5°, a correction of 0.0058 may be made for each degree. Hehner regards the table of specific gravities prepared by Lenz as the most accurate. The determinations were made at 12-14°. By use of the factor mentioned above Richmond has recalculated Lenz's table to 15.5°.

PERCENTAGE	SPECIFIC GRAVITY AT 15.5°	PERCENTAGE	SPECIFIC GRAVITY AT 15.5°
100	1.2674	87	1.2127
99	1.2647	86	1.2501
98	1.2620	85	1.2274
97	1.2594	84	1.2148
96	1.2567	83	1.2122
95	1.2540	82	1.2196
94	1.2513	81	1.2169
93	1.2486	80	1.2143
92	1.2460	79	1.2117
91	1.2433	78	1.2090
90	1.2406	77	1.2064
89	1.2380	76	1.2037
88	1.2353	75	1.2011

See vol 1, page 21, for Squibb's method of determining specific gravity.

Lewkowitsch (*Chem Anal of Oils, Fats and Waxes*, p 793) prefers the following method.—The sample is warmed in a closed bottle by immersing in warm water until all air-bubbles have collected at the top. The glycerol is then allowed to cool in the cooled bottle, preferably to the normal temperature, and then carefully filled into the ordinary specific gravity bottle provided with a perforated stopper. If this has been pushed home, after the last filling, the very small drop of glycerol squeezed out is wiped off with a linen cloth and the bottle taken out of the water-bath. The determination may be made exact to the fourth decimal if the weights are reduced to vacuum. Complicated calculation is avoided by determining once for all the necessary corrections for the pycnometer when filled with water. Suppose the weight  $p$  has been found in air, then the corrected weight  $P$  will be.—

$$P = p + pR$$

For brass weights, the correction *R* for the specific gravities likely to occur is found from the following table:—

SPECIFIC GRAVITY	CORRECTION (P)	SPECIFIC GRAVITY	CORRECTION (R)
1.00	0.00100	1.10	0.00095
1.02	0.00103	1.15	0.00090
1.04	0.00101	1.20	0.00086
1.06	0.00099	1.25	0.00082
1.08	0.00097	1.30	0.00078

The determination of the specific gravity is still available for the estimation of glycerol in presence of neutral salt-, both inorganic and organic, provided that proper allowance be made for the influence on the specific gravity of the liquid exerted by the salts present.

#### ISOLATION OF GLYCEROL

In very many cases the determination of glycerol by direct weighing or by the observation of the specific gravity of the solution is inapplicable, owing to the presence of foreign matters the quantity or influence of which cannot be ascertained or allowed for. Under such circumstances it is often requisite to isolate the glycerol in a state of approximate purity. This can frequently be effected qualitatively in a very satisfactory manner, but it too often happens that the evaporations which are necessary steps in the process cause such a loss of glycerol by volatilisation as to render the result of little value. Albuminous and some other foreign matters may be separated from a solution containing glycerol by adding a solution of basic lead acetate, and subsequently removing the excess of lead from the filtered solution by means of hydrogen sulphide. This method may be employed for the analysis of the pharmaceutical preparations known as "glycerol of tannic acid" and "glycerol of gallic acid," and is useful as one stage of the treatment of soap lyes for the determination of glycerol.

Albuminous and some other organic matters can often be removed completely by precipitating the slightly alkaline solution with zinc chloride. The precipitate is filtered off and the filtrate rendered faintly acid, when a further precipitation will often occur. The last traces of zinc may be removed from the solution by potassium ferri-cyanide, which is also a very perfect precipitant of albumin.

Dilute glycerol may be further purified by evaporating off the water at as low a temperature as possible, and treating the residue with absolute alcohol, a mixture of alcohol and ether, or a mixture of alcohol



and chloroform, according to circumstances. Absolute alcohol readily dissolves glycerol, while many classes of salts (e.g., metallic sulphates, phosphates, tartrates, &c.) are insoluble. The alkali-metal chlorides are not completely separated by alcohol alone, but a mixture of equal measures of absolute alcohol and dry ether leaves them undissolved. The same solvent serves to separate glycerol from sugar, but the use of a mixture of two measures of absolute alcohol with one of chloroform is preferable. If the filtered solution be treated with about twice its measure of water, the chloroform separates from the diluted alcohol, and often carries troublesome coloring matters with it.

Any process of determining glycerol which involves the evaporation of an aqueous or alcoholic solution and isolation of the glycerol in substance is deficient in quantitative accuracy, as evaporation of glycerol in the latter end of the concentration is unavoidable, and the loss from this cause is often very considerable. Even absolute glycerol is sensibly volatile at 100°, the loss of weight varying with the mode of heating, the shape and material of the containing vessels, and the surface exposed.

The following figures, due to Nessler and Barth (*Zeits. Anal. Chem.*, 1884, 323), show the rate of evaporation of glycerol under different conditions. The experiments were made with glycerol which had been heated for six hours over a water-bath at 100° C., and then for six hours longer in an air bath heated to 100°. In one series of experiments the glycerol was exposed in a water oven at 100° C. in a platinum dish 20 mm. high and 80 mm. diameter at the top, and 60 at the bottom; in the other, it was heated in a beaker of thin glass 40 mm. high and 48 mm. in diameter —

	PLATINUM DISH	GLASS BEAKER
1 gm. lost, in first 2 hours,	46 mgrm	36 mgrm
" " in second 2 hours,	29 "	14 "
" " in third 3 hours,	21 "	5 "
Average for last 3 hours,	7 "	17 "
0.5 gm. lost in first 2 hours,	36 "	45 "
" " in second 2 hours,	28 "	11 "
" " in third 3 hours,	24 "	6 "
Average for last 3 hours,	7.7 "	2 "

The following figures show the loss of weight when heated on an open water-bath kept briskly boiling —

	PLATINUM DISH	GLASS BEAKER
1 gm. lost, in 1 hour,	37-39-29-30 mgrm	30-18 mgrm
0.5 " " "	34-29-21-30 "	11- 2 "

Other experiments conducted in platinum and glass vessels of various diameters showed that the loss increased with the diameter of the vessel (*i.e.*, with the surface of glycerol exposed), and that the rate of evaporation was less in a vessel composed of a material of low conducting power.

The volatilisation of glycerol during the evaporation of an aqueous liquid may be prevented by adding an excess of lime, which forms a compound with it, but Clausnizer has shown (*Zeits Anal. Chem.*, 1881, 58) that from the product the glycerol cannot be dissolved by absolute alcohol, and if hydrated alcohol be employed, caustic alkalies resulting from the reaction of the lime on phosphates may pass into the alcoholic liquid, and carry with them bodies not otherwise soluble. Even if excess of lime be avoided, the glycerol cannot be extracted completely from the residue by cold alcohol or ether-alcohol. For the determination of the glycerol contained in beer and similar liquids, Clausnizer recommends the following process, which is essentially the same as that for the determination of glycerol in wine, described in volume 1, page 80—50 c.c. of the liquid are evaporated at 100° in a dish containing a previously tared glass rod. As soon as the carbon dioxide has escaped, about 3 gm. of slaked lime should be added and the whole evaporated to a syrup, when about 10 gm. of coarsely-powdered marble should be stirred in, and the stirring repeated occasionally during the drying, until hard lumps remain. The dish is then reweighed, the contents rubbed to powder, and an aliquot part ( $\frac{1}{2}$  or 1) thoroughly extracted in a Soxhlet-tube with 20 c.c. of rectified spirit. The alcoholic extract is mixed with 25 c.c. of dry ether, and after standing for an hour is filtered into a small weighed flask, and the filter and precipitate washed with ether-alcohol (3:2). The flask is placed in an oblique position on a gently heated water-bath, until the ether and alcohol are removed, and the residue is then dried in the lightly covered flask at 100°, until the loss is not more than .002 gm. in two hours, which occurs in from 2 to 6 hours. After weighing the glycerol, it is desirable to wash it with a little alcohol into a platinum dish, evaporate, and ignite. The weight of the ash obtained is deducted from that of the impure glycerol previously found.

The foregoing process possesses the advantage of general applicability, and may be modified as required for particular purposes.

To determine the glycerol resulting from the saponification of a fixed oil, J. David (*Compt. Rend.*, xiv. 1477) takes 100 gm. of the oil or fat, heats it moderately in a porcelain dish, and adds 65 gm. of crystallised barium hydroxide, with brisk stirring. When most of the

water is expelled the heating is discontinued. 50 c.c. of very strong alcohol is then poured on the mass, and the whole well stirred, when 1 litre of water is added, and the whole boiled for one hour. The insoluble barium soap is filtered off and washed twice with cold water; the filtrate faintly acidulated with sulphuric acid, again filtered, and the filtrate concentrated to about half its measure. A small quantity of barium carbonate is then added to remove the last traces of sulphuric acid, the liquid again filtered, and the filtrate evaporated to 5 c.c. at a low temperature, when the contained glycerum is deduced from the density of the liquid. If desired, the liquid can be further concentrated, and the glycerol extracted with ether-alcohol, &c.

The objection has been raised to this and similar methods that saponification of some fats by barium hydroxide is not complete.

A process proposed by H. Raynaud for the estimation of glycerol in wine might probably be applied to the assay of *spent lyes* and *crude glycerol*. The liquid is concentrated to a small bulk and then treated with a large excess of alcohol and hydrofluosilicic acid. The liquor is filtered from the insoluble alkali-metal silico-fluorides, the precipitate washed with alcohol, and the filtrate treated with a slight excess of barium oxide, mixed with sand, and evaporated *in vacuo*. The residue is extracted with a mixture of equal volumes of alcohol and ether, the solution evaporated and the residual glycerol weighed after being dried in a vacuum for twenty-four hours over phosphoric anhydride. Any ash left on igniting the isolated glycerol is deducted from the original weight. The method might be materially shortened by adding silver sulphate drop by drop to the liquid filtered from the barium silicofluoride, as long as a precipitate is produced. By this means a mixed precipitate of barium sulphate and silver chloride would be obtained, and the filtrate, after evaporating off the alcohol, would be practically pure dilute glycerol, the strength of which could be deduced from the specific gravity.

#### DETERMINATION OF GLYCEROL BY CHEMICAL METHODS

All the foregoing methods of determining glycerol aim at isolation of the substance in an approximately pure state, or mixed with water and saline matters only. The following processes, on the other hand, are based on the chemical reactions of glycerol.

Morawski (*Jour. f. Pract. Chem.*, xxii, 401) has described a method of determination based on the fact that, on heating glycerol with litharge, a solid monoplumbic glyceride is formed, of the composition  $C_3H_5PbO_2$ , one molecule of water being eliminated. Muter's process

(*Analyst*, 1881, 41) is based upon the solubility of copper hydroxide in potassium hydroxide and glycerol. Boulez's method is based upon the conversion of the glycerol into calcium glycerophosphate, and that of Diez upon its conversion into benzoate. All these furnish results less accurate than the oxidation and acetic methods about to be described. That of Hehner, depending upon the oxidation of the glycerol by potassium dichromate, is perhaps the most satisfactory on the score of general applicability, accuracy and ease in manipulation.

H. G. von Töring estimates the glycerol in brandy lyes as follows. The liquid is filtered and 30 c.c. are evaporated on the water-bath to 5 c.c. 15 gm. of burnt gypsum are mixed with the residue, and when the mass begins to set it is well powdered and exhausted for six hours with alcohol in an extraction apparatus. The alcoholic solution is treated with 10–20 c.c. of water and heated until all the alcohol is driven off, when the residue is distilled. The distillation apparatus consists of a retort resting in an air-bath, and a Liebig's condenser. The receiving flask has a neck connected with an air-pump. The distillation is at first carried on at 150°–170° without working the air-pump, until all the water has passed over into the receiver. The pump is then set to work and the temperature raised to 190°–210°. When all the glycerol has come over, about 3 to 4 c.c. of water are added to the contents of the retort, and distilled at 150°–170° under ordinary pressure in order to wash all the glycerol into the receiver. The yellowish distillate, amounting to 10 or 15 c.c., is mixed in the receiver with 5 c.c. of benzoyl chloride and 35 c.c. of a 10 per cent solution of sodium hydroxide with frequent cooling and shaking to consolidate the precipitated benzoic ester, which is finally collected on a weighed filter, washed with water, dried for two to three hours at 100° C. and weighed (3.85 gm. = 1 gm. glycerol).

The estimation of the glycerol in the distillate would be preferably made by Hehner's method (see below). The separation of glycerol from non-volatile matters by distillation *in vacuo* appears to be capable of useful application.

*Permanganate Oxidation Process*.—The estimation of glycerol may be effected by oxidation to oxalic acid by an alkaline solution of potassium permanganate, the reaction being—



The process was originally suggested by J. A. Wanklyn and further worked out by W. Fox and Benedikt, and Zsigmondy. It has been

fully investigated by J. C. Belcher and the author, and is found to give very accurate results in the absence of alcohol and other foreign bodies yielding oxalic acid on oxidation. The best way of operating is to saponify 10 gm of the oil at 100° C with 4 gm of potassium hydroxide dissolved in 25 cc of water in a securely closed bottle, which is agitated from time to time. After ten or twelve hours, or when all oily globules have disappeared, the contents of the bottle are diluted with hot water, when a perfectly clear solution should be obtained (Except in the case of sperm oil, waxes, and other bodies yielding insoluble higher alcohols on saponification, it is extremely difficult to effect the complete saponification of such bodies by aqueous alkali, and methyl-alcohol must be resorted to, of such purity that it does not yield oxalic acid by oxidation with alkaline permanganate). The soap solution is then decomposed by a moderate excess of sulphuric acid, the liberated fatty acids separated, and the aqueous liquid, which must be perfectly clear and free from suspended oily globules, made up to known measure. One-half (= 5 gm of oil) is diluted in a porcelain basin with cold water to 400 cc, from 10 to 12 gm of potassium hydroxide added, and then a saturated solution of potassium permanganate till the liquid is no longer green, but blue or blackish. It is then heated gradually and boiled for one hour, when a strong solution of sodium sulphate is added till all violet or green color is destroyed. The liquid and contained precipitate are poured into a 500 cc flask and hot water added to 15 cc above the mark, as an allowance for the volume of the precipitate and the increased measure of the hot liquid. The solution is passed through a dry filter, and when cool, 400 cc (= 4 gm of oil) measured off, acidified with acetic acid, and precipitated by calcium chloride. When the precipitate has completely deposited, it is filtered off and washed with hot water. It consists chiefly of calcium oxalate, but is liable to contain calcium sulphate, silicate, and other impurities. It may be ignited and the amount of oxalate deduced from the carbonate formed, but a preferable plan is to test it with dilute sulphuric acid, rinse it off the filter, and titrate the diluted liquid at about 60° C with a decinormal solution of potassium permanganate (3.162 gm of  $\text{KMnO}_4$  per litre), each cc of which corresponds to 0.045 gm of anhydrous oxalic acid or 0.046 gm of glycerol. The results obtained by this process are satisfactory. Certain acids of the acrylic or oleic series, and possibly oleic acid itself, yield oxalic acid by alkaline oxidation; but the higher members of the series (*e.g.*, oleic acid) are insoluble in water, and the lower are not known to occur in fixed oils under normal con-

ditions. The bodies formed by the oxidation of linseed oil render the process wholly useless for the determination of glycerol in such products.

Herbig has suggested the use of hydrogen dioxide in place of sulphite, and employs a smaller quantity of potassium permanganate. Mangold (*J. S. C. I.*, 1891, 803) reports favorably on the method, and recommends the following procedure:—To 0.2–0.4 gm. of glycerol, dissolved in 300 cc water containing 10 gm. potassium hydroxide, as much of a solution containing 5 per cent. potassium permanganate is added as will correspond to 1.5 times the theoretical quantity of glycerol (for 1 part glycerol 6.87 parts of potassium permanganate). The operation is conducted in the cold and the solution must be agitated on addition of the permanganate. After standing for about half an hour at ordinary temperature, sufficient hydrogen dioxide is added to completely decolorize the liquid. The whole is now made up to 1000 cc, well shaken, and 500 cc filtered through a dry filter. After heating the filtrate for half an hour to destroy all hydrogen peroxide, and cooling to about 60° C, sulphuric acid is added and the liquid titrated with permanganate. Heating after addition of the permanganate is superfluous. A number of results of analysis by the above method are given, which prove it to be accurate even in the presence of 90 per cent of butyric acid.

*Hehner's Method*—Glycerol, when heated with potassium dichromate and sulphuric acid, is quantitatively oxidised to carbon dioxide. Cross and Bevan and Legler make use of this fact to estimate the glycerol by measuring or weighing the evolved carbon dioxide. A more convenient method is that of Hehner (*J. S. C. I.*, 1889, 4), which is based upon a determination of the dichromate reduced. The reagents and operation are as follows:—

1. Potassium dichromate solution, containing in each litre about 74.86 gm. of potassium dichromate and 150 cc of strong sulphuric acid. The exact oxidising value of the solution must be ascertained by titration with solutions of known quantities of iron wire or pure ferrous ammonium sulphate.

2. Ferrous ammonium sulphate solution containing about 240 gm per litre.

3. Potassium dichromate solution one-tenth the strength of No. 1. The ferrous solution is exactly standardised upon the stronger dichromate solution, 1 cc. of which should correspond to 0.01 gm. glycerol.

With pure glycerol, the oxidation is absolutely quantitative. Crude glycerols must be treated as follows:—For the removal of chlorine and

of aldehydic compounds some silver oxide is added to a weighed quantity of the sample (about 1.5 gm.), which is placed in a 100 c.c. flask. After slight dilution the sample is allowed to stand with the silver oxide for about ten minutes. Basic lead acetate is then added in slight excess, the bulk of the fluid made up to 100 c.c., and a portion filtered through a dry filter, 25 c.c. of the filtrate are placed in a beaker previously well cleaned with sulphuric acid and potassium dichromate to remove all traces of fat, from 40 to 50 c.c. of the standard dichromate are added, accurately measured, and about 15 c.c. of strong sulphuric acid, and the beaker, covered with a watch-glass, is heated for two hours in boiling water. After that time the excess of dichromate is titrated back with ferrous ammonium sulphate solution.

As the dichromate solution is necessarily a somewhat strong one, the measuring must be done with the greatest care, some attention being paid to the temperature. [Hehner has found that a dichromate solution of the strength indicated expands for each degree C. 0.5 per cent.] The results upon repetition agree well. The method is easy and rapid. It is open to the objection that by precipitation by lead the impurities may not be perfectly removed, anything left being oxidised and counted as glycerol. However, all higher fatty acids and all resin acids, as well as albuminoids, sulphides, thiocyanates, and aldehydes, are completely removed, and the lower fatty acids, such as acetic and butyric, are not attacked by chromic acid. Hehner (*J.S.C.I.*, 1889, 4) has made a careful comparison of the dichromate and the acetin methods (see below), and finds the results to agree very closely, the differences in most cases being within the range of experimental error. To ensure the greatest amount of accuracy, he advises the use of both methods upon the sample to be analysed, the mean of the two results being taken. In the case of very dilute liquors, such as unconcentrated soap-lyes, previous concentration of the sample to about 50 per cent. of the glycerol is necessary with the acetin method, which fails when the proportion of glycerol falls as low as 30 per cent. In such cases the dichromate method is preferred.

The estimation of glycerol in *fats* and *soaps* is carried out as follows. Saponify about 3 gm. of the fat with alcoholic potassium hydroxide; do not drive off the alcohol, but dilute the soap solution to about 200 c.c.; decompose with dilute sulphuric acid; filter off insoluble acids, which may be estimated as usual. Vigorously boil the filtrate and washings, amounting altogether to about 500 c.c., in a covered beaker down to one-half, then add sulphuric acid and standard dichromate as

described. The following are some results obtained by Hehner and Mitchell in this way —

	GLYCEROL
Olive oil, . . . . .	10 26
Cod-liver oil, . . . . .	9 87
Linseed oil, . . . . .	10 24
Margarine, . . . . .	10 01
Butter, . . . . .	12 4
„ . . . . .	11 96

The *acetin method* of Benedikt and Cantor (*J S C I*, 1888, 696) depends upon the formation of acetin (trityl acetate) when glycerol is heated with acetic anhydride. Lewkowitsch (*Chem Zeit.*, xiii 659) has shown that the method gives closely concordant results in the case of moderately pure "crude glycerins," and recommends its adoption in all cases in which the glycerol is first isolated in a fairly pure state as in its determination in fats and oils. The fat is saponified, the resultant soap is decomposed with sulphuric acid, and the fatty acids separated by filtration. Excess of barium carbonate is added to the filtrate, which is then evaporated on the water-bath until most of the water has been driven off. The residue is exhausted with a mixture of ether and alcohol, which is then driven off by a gentle heat.

For the determination, 1 to 1.5 gm. of this crude glycerol is heated for 1 to 1½ hours in an inverted condenser with 7 or 8 gm. of acetic anhydride and about 3 gm. of anhydrous sodium acetate (previously dried in an oven). It is allowed to cool, 50 c.c. of water are added, and the heating is continued (still with the condenser, as acetin is volatile in a current of steam) until it begins to boil. When the oily deposit at the bottom of the flask is dissolved, the liquid is filtered from a white flocculent precipitate, which contains most of the impurities of the crude glycerol, allowed to cool, phenolphthalein added, and dilute sodium hydroxide (about 20 gm. per litre) run in until neutrality is obtained. Care must be taken not to exceed that point, as acetin is easily saponified.

During the operation the solution must be agitated continually, so that the acid may not be in excess locally any longer than is unavoidable. The point of neutrality is reached when the solution becomes reddish-yellow. It must not be allowed to become pink. The determination is quite inaccurate if the solution is overneutralised even for the shortest time. 25 c.c. of strong sodium hydroxide (about 10 per cent. strength) are now added from a pipette. The mixture is then heated for fifteen minutes and the excess of alkali titrated back with



normal or half-normal hydrochloric acid. The strength of the alkali used is determined at the same time by titrating another 25 c.c. measure with the same pipette. The difference between the two titrations gives the amount of alkali consumed in saponifying the acetin, and from this the quantity of glycerol is calculated.

### Commercial "Glycerin."

In practice, glycerol is always obtained by the saponification of fats; all sources yield the same variety of glycerol, and not isomers or homologues of the ordinary body. On the large scale, especially when the saponification is effected by the autoclave process, the proportion of glycerol obtained is very notably less than the theoretical yield, the loss being due in part to incomplete saponification, largely to loss by volatilisation, which is wholly disregarded, and very probably in part to decomposition of the glycerol into formic acid and other products.

For the saponification of fats with a view of obtaining glycerol, a variety of agents has been employed. Formerly olive oil was boiled with water and lead oxide, but at a later date this was replaced by lime. Superheated steam has been employed to effect the saponification, as also has strong sulphuric acid. Glycerol obtained from the waste waters of the acid-saponification process is known as "distillation glycerin." It contains mineral matter to the extent of 3 per cent. or more, and organic impurity may be present to an equal extent. Tested with basic lead acetate such glycerins give a copious precipitate. Hydrochloric acid also causes turbidity due to the separation of fatty acids.

At present the bulk of the glycerol of commerce is either a secondary product of the soap-works, and hence is produced by saponification with caustic soda, or results from the saponification of fats under high pressure with water and a limited proportion of a base. This last must be considered the principal method of obtaining glycerol on a manufacturing scale, and is ordinarily carried out as follows.—The fat, which is commonly a mixture of palm oil and tallow, is heated for from 2 to 4 hours in an autoclave with 2 or 3 per cent. of lime and about one-third of its measure of water, under a pressure of 8 atmospheres, some steam being allowed to escape so as to keep the mixture in agitation. The product is then blown out into a tank, and the "sweet water" or dilute glycerol drawn off. The lime soap is decomposed with dilute sulphuric acid, and the resultant fatty acids further treated by pressure or distillation. The "sweet water" is then concentrated to a specific gravity of 1.24, when it forms a liquid of brownish color

known as "raw glycerin" or "saponification glycerin," and contains about 90 per cent glycerol. It gives but a slight precipitate when tested with basic lead acetate, and in samples of good quality hydrochloric acid causes no turbidity. It is further purified by filtration through animal charcoal, followed by distillation with superheated steam at a temperature not exceeding 230° C. The lime ordinarily employed for the saponification has been successfully replaced by about  $\frac{1}{2}$  per cent of zinc oxide or zinc grey, the reducing action of the latter body being said to prevent the discoloration of the product.

The recovery of glycerol from spent soap-makers' lyes has acquired much importance, and a number of patents have been obtained to effect this object. The spent lye usually contains water; glycerol, sodium chloride, sulphate, and carbonate; a small quantity of sodium hydroxide; and variable amounts of resinous, fatty, and albuminous matters. Some samples contain a considerable quantity of thiosulphates (hypo-sulphites) besides sulphides, thiocyanates, cyanides, and ferrocyanides. The glycerin obtained on concentrating such lyes is often quite unfit for distillation. C. T. Kingzett gives the following as the average composition of the lye after concentration to a specific gravity of 1.36 —

Water,	7.53 lbs per gallon
Glycerol,	2.04 " "
Salts,	2.78 " "
	<hr/> 12.35

The salts deposited from the lye during concentration contain 78 per cent. of sodium chloride, with smaller proportions of sodium sulphate and carbonate, glycerol, water, &c.

The glycerin obtained from soap-lyes has usually a specific gravity of about 1.3, and yields about 10 per cent. of ash, which in samples of good quality consists largely of salt. The amount of organic impurity varies greatly. In addition to the salt already mentioned, the lower grades may contain notable proportions of sodium hydroxide, carbonate, sulphate, thiosulphate, and thiocyanate.

Samples of good quality should contain from 80-82 per cent of glycerol, and should not become turbid on addition of hydrochloric acid.

After concentration the crude glycerol still contains a considerable proportion of salts, besides other impurities. To remove these it is subjected to distillation with the aid of superheated steam, but the product often requires a repetition of the process to effectually remove the sodium chloride and other foreign matters.

Distilled glycerol often possesses a disagreeable acid taste, and hence it is sometimes further purified by freezing, which may be effected by cooling the concentrated liquid to  $0^{\circ}\text{C}$  and adding a crystal of solid glycerol. This induces solidification, and the resultant crystals are separated from the still liquid portion by a centrifugal machine.

By far the largest application of glycerol is for the manufacture of nitroglycerin (page 333), but it is also employed extensively in the manufacture of toilet soaps, filling gas-meters in situations liable to be exposed to great cold, and in pharmacy and medicine.

#### ANALYSIS AND ASSAY OF COMMERCIAL GLYCEROL.

Commercial glycerol is liable to contain a variety of impurities due to its method of manufacture,—the article made from waste lyes being especially impure. Lead and other heavy metals, calcium compounds, sodium chloride, sulphate, thiosulphate, and sulphide, cyanogen compounds, organic acids, rosin products, and other organic bodies of an indefinite nature, are the impurities most frequently present. In addition, glycerol has been sometimes intentionally adulterated. Solutions of cane sugar, glucose, and dextrin have been occasionally used for this purpose, and a saturated solution of magnesium sulphate mixed with glucose has also been employed.

The following systematic method may be employed for examining commercial glycerol for impurities and adulterants, but except in rare instances it is unnecessary to make the examination so exhaustive, as a knowledge of the history of the sample or of the purpose for which it is intended suffices to limit the number of impurities for which a search requires to be made. Thus, the impurities present in the raw material are much greater in number and amount than those present in the distilled product, and, of the former, that from soap-lyes is much more impure than the product resulting from the autoclave process. The distilled product, again, varies much in character according to its origin, and requires examination for particular impurities according to its intended application in pharmacy, petroleum, the manufacture of nitroglycerin, &c.

a. The color of the commercial article affords no accurate criterion as to whether it is raw or has been once distilled, for, although the raw product is usually very highly colored, pale samples are often met with, especially those produced by the lime process of saponification, while, on the other hand, once-distilled samples from soap-lyes are not uncommonly very dark. In general, however, raw glycerin varies in

color from light brown to nearly black, and distilled from brown to colorless.

b. The specific gravity of commercial glycerol may be observed by means of the Westphal balance, and in some specifications this method of determination is insisted on, the indications of the hydrometer being sometimes two or three degrees in excess of the truth. In the absence of foreign matters, or even in the presence of certain foreign matters, the nature and amount of which are known or can be ascertained and duly allowed for, the specific gravity determination affords a very satisfactory means of determining the percentage of glycerol present in commercial samples (see pages 288, 289). Thus, a correction may be made for the mineral matter present by gently igniting a known measure of the sample without burning off the whole of the carbon, treating the residue with a little acetic acid to dissolve any carbonates which may have been formed from the salts of organic acids, evaporating to dryness at  $100^{\circ}$ , dissolving the residue in water, and making up the solution to a volume equal to that used for the experiment. The specific gravity of this solution is deducted from that of the original sample before deducing the percentage of glycerol from the latter. Thus, if the original sample has been found to have a specific gravity of 1.220, while the specific gravity of the solution of the ash is 1.035, then the difference between the two ( $= 0.185$ ) is the increase due to the glycerol present, and this figure divided by 2.665 will give the percentage of glycerol in the sample. Organic matters will by this method be reckoned as glycerol, but if separately determined by means of basic lead acetate (page 325) a correction may be made for them.

The specific gravity of the twice distilled product of a high degree of purity sometimes reaches the extreme figure of 1.267, but ordinarily is rarely above 1.261. The specific gravity of commercial glycerol does not necessarily indicate whether the sample is raw or distilled, although the former is usually of higher specific gravity, owing to the presence of saline and foreign organic matters. The raw glycerin from soap-lyes may be boiled down to a specific gravity of 1.320, or even 1.360, but the specific gravity of the product from the autoclave process, or from lime or sulphuric acid saponification, is always less than this.

c. The proportion of *mineral matter* affords a good indication of the nature of the sample. 5 grm. or 5 c.c. of the sample should be heated in a porcelain crucible till it inflames, when the source of heat is removed and the glycerol allowed to burn away spontaneously.

The distilled product burns quietly, but with raw glycerin more or less sputtering is observed. A distilled product of good quality will leave a mere trace of carbonaceous residue on ignition, any considerable black residue indicating the presence of serious *organic impurity*. On igniting the residue *at the lowest possible temperature*, the *mineral impurities* remain and may be weighed.

Treated in this manner, a distilled glycerol never yields more than 0.2 per cent of ash, and rarely as much as 0.1 per cent, while even the best samples of the raw material show a considerably larger proportion. In that obtained from soap-lyes the ash usually ranges from 7 to 14 per cent, a considerable proportion consisting of sodium chloride, and more or less sulphate, carbonate, silicate, &c, being also present; but if Fleming's dialysis process has been employed, the mineral matter usually averages from 6 to 7 per cent. In the crude product from the autoclave process or from lime saponification the percentage of mineral matters, though variable, is much lower than in glycerin from soap-lyes, the specific gravity being also correspondingly low. The presence of traces of lime, magnesia, or zinc oxide in the ash will indicate the nature of the base used for saponifying.

d. Although sufficiently accurate for commercial purposes, the ignition of the residue left on combustion does not always give the true amount of mineral matter present in the sample, owing to unavoidable volatilisation of sodium chloride if the ignition be continued until the carbon is completely consumed. Lewkowitsch prefers to cautiously char 3-5 gm. at a temperature just sufficient to destroy the organic matter. After cooling, the char is exhausted with water and transferred to a filter, the filtrate evaporated in a platinum dish on the water-bath, and the residue, which must be white, heated (not above 400° C.) and weighed. The carbon on the filter may, as a rule, be disregarded, unless the sample contains large proportions of lime.

A method which gives very good *comparative* results is to treat the charred mass with a few drops of strong nitric and sulphuric acids, and ignite, when the chlorides will be converted into the less readily fusible and volatile sulphates. If desired, the weight thus obtained can be corrected by multiplying the weight of chlorine found in an equal quantity of the sample by 1.352, and deducting the product from the weight of the "sulphated ash." Richmond treats the charred mass with a few drops of sulphuric acid and heats the residue over a good Bunsen flame until white. The sulphated ash multiplied by 8 agrees fairly well with the ash found without sulphating.

e. The weight of the ash having been ascertained, it may be further

examined for lead, iron, zinc, magnesium, calcium, carbonates, chlorides, sulphates, &c. If the ash has been "sulphated," no carbonates or chlorides will be present, while the existence of sulphates is, of course, certain. The ash may be conveniently examined by treating it with dilute sulphuric acid, when the *copper, iron, zinc, magnesium*, and more or less *calcium* will be dissolved as sulphates, and can be detected in the solution by the usual methods. The residue will contain lead sulphate, together possibly with calcium-sulphate. On treating it with a hot solution of ammonium acetate, the lead sulphate will be dissolved, and the resultant solution will give a yellow precipitate with potassium chromate and a black precipitate with hydrogen sulphide.

*f Calcium* is a frequent impurity occurring most commonly as calcium oleate. It is most readily determined by precipitating the diluted sample with ammonium oxalate. Precipitation in an alcoholic solution with sulphuric acid has been recommended by Cap, but presents no advantages over the oxalate method.

*g Alkalinity* in commercial glycerol is due almost entirely to sodium carbonate, and is readily determined by titrating the diluted sample with standard acid. Sulman and Berry recommend the use of litmus as an indicator, neither phenolphthalein nor methyl-orange giving sharp end-reactions. Crude glycerol from soap-lyes is purposely alkaline owing to the risk of concentrating it in presence of acid. The alkalinity usually varies from 0.5 to 2.0 per cent, depending to some extent on the manner in which the lyes have been treated. In a case cited by Fleming, in which the glycerin had been separated from the lye by alkali instead of salt, the resulting glycerin contained 31 per cent of sodium carbonate.

*h Chlorides* cannot be determined by direct titration or precipitation with silver, owing to the solubility of silver chloride in glycerol and the reduction of the nitrate by various impurities. The determination is best made by allowing a weighed portion to burn away as already described, exhausting the carbonaceous residue with water, and titrating the filtered solution with decinormal silver nitrate, using neutral potassium chromate as an indicator. Crude soap-lye glycerins usually contain from 5 to 10 per cent of salt.

*i Sulphates* may be determined by precipitating the diluted sample with barium chloride. They are usually present in the product from soap-lyes, and sometimes in very large amount. Glycerins obtained by saponifying fat with sulphuric acid are always charged with sulphates, and often contain *sulphites*, while appreciable quantities of

*thiosulphates* and *sulphides* are occasionally present, the last three being objectionable. The milky precipitate produced on acidifying the raw product from soap lyes sometimes contains a considerable proportion of free *sulphur*, the proportion amounting in some cases to 40 or even 60 per cent. of the whole precipitate. Such samples will yield objectionable volatile sulphur compounds on distillation.

C. Ferrier (*J. S. C. I.*, 1893, 471) proposes the following method for detecting sulphur compounds.—The sample is diluted with ten times its volume of water and neutralised with hydrochloric acid. This mixture is treated at from 60° to 70° C with about three per cent. of the carbon residue from the manufacture of potassium ferrocyanide (which has been previously washed with dilute nitric acid and water and heated to redness in a closed crucible). One drop of the solution after treatment with the purified carbon residue is placed on a strip of paper saturated with lead nitrate. If no yellow stain appears, the sample contains less than 0.001 part of sulphides. To detect a still smaller quantity, the sample is heated in a small flask with a few drops of hydrochloric acid and a little sodium carbonate held over the mouth of the flask.

To detect *thiosulphates* and *sulphites* a few c.c. of barium chloride solution are added to the solution of the sample, and the liquid filtered. Barium sulphite is precipitated and the *thiosulphates* may be found in the filtrate, which, on addition of potassium permanganate to the acidified solution, will become cloudy, even in the presence of only 0.001 part of *thiosulphate*.

The presence of sulphite in the precipitate is proved by washing it repeatedly with boiling water, then adding to the remaining precipitate a few drops of starch and iodine solution; in presence of sulphites the blue coloration will gradually disappear. See also Richardson and Aykroyd (*J. S. C. I.*, 1896, 171) for the quantitative estimation of these compounds.

*k Organic Impurities* of various kinds occur in crude glycerol, and are mostly of a very objectionable character. Their sum (including albuminous and coloring matters, resin products, and higher fatty acids) may be determined with a fair approach to accuracy by Sulman and Berry's modification of a method devised by Champion and Pellet. Fifty gm. of the sample are diluted with twice its measure of water, carefully neutralised with acetic acid, and warmed to expel carbonic acid. When cold, a solution of basic lead acetate is added in slight but distinct excess, and the mixture well agitated. The formation of an abundant precipitate, which rapidly subsides, is an indication of

considerable impurity in the sample. To ascertain its amount the precipitate is first washed by decantation and then collected on a tared, or preferably a double counterpoised, filter, where it is further washed, dried at  $100^{\circ}$  to  $105^{\circ}$  C., and weighed. The precipitate and filter paper are then ignited separately in porcelain, at a very low red heat, the residues moistened with a few drops of nitric acid and re-ignited. The weight of the residual lead oxide (and sulphate) deducted from that of the original precipitate gives the weight of *organic matter* precipitable by lead. The proportion obtained from raw glycerins is extremely variable, but the amount present in the distilled product should not exceed 0.5 to 1.0 per cent.

Lewkowitsch determines the *total solid residue*, including *polyglycerols*, by allowing a weighed quantity of the sample to evaporate gently at  $160^{\circ}$  C. Care should be taken not to heat too rapidly, otherwise even pure glycerol may become polymerised. A few drops of water added from time to time will assist in the volatilisation of the glycerol. The weight of the residue is taken and that of the ash, subsequently found, is deducted. The difference (the "organic residue") gives a fair indication as to the care with which the article has been manufactured. Lewkowitsch found from .024 to .05 per cent. in seven samples of "chemically pure" glycerin of good quality. In four samples, unfit for pharmaceutical purposes, .07 to .09 per cent. was found.

Precipitation with basic acetate of lead is a valuable preparation for subsequent analytical examination, and is almost essential before some of the methods of determining glycerol and sugar are applied. When the precipitation is effected with this object, it is convenient to make up the liquid to a definite bulk and pass it through a dry filter, or allow the precipitate to settle in a Muter's tube (fig. 10, page 247), subsequently operating on a known proportion of the total solution. This plan obviates the necessity of washing the precipitate and the objectionable dilution of the liquid caused thereby.

In some cases it is of interest to distinguish between the various organic matters precipitable by lead, as they are not all equally objectionable. This object may to some extent be effected as follows —

1. *Albuminous matters*, derived from the envelopes of the fat-globules, are nearly always present to a greater or less extent, the product from soap-lyes containing the largest proportion, owing to the solvent action of the alkali on the proteid matters of the fats saponified. They are objectionable on account of the mechanical difficulties they occasion



during the subsequent distillation, and the contamination of the distillate with empyreumatic and colored products. An approximate determination of the albuminous matters may be made by precipitating with basic lead acetate, as already described, and determining the nitrogen by the Kjeldahl method. The nitrogen, multiplied by 6.25, gives the amount of albuminous matter in the precipitate.

*m Rosin* is a very frequent and objectionable impurity in the product from soap-lyes, but is absent from that from candle-works. A portion of the rosin is precipitated on acidulating, but the use of basic lead acetate is better. When rosin is present, the distillate often has a strongly-marked fluorescence from the presence of rosin oil. This impurity may be further detected and removed by agitating the sample with ether or petroleum spirit, which, after separation and evaporation, leaves the rosin oil in a form recognisable by its physical characters, taste, and odor on heating.

*n. Higher fatty acids*, chiefly *oleic acid*, are not unfrequently present in glycerol from soap-lyes, even after distillation, and are very objectionable in a product intended for making nitroglycerin. If the amount of fatty acids be considerable, mere dilution with water causes their precipitation, but smaller quantities may be detected by diluting the glycerol and passing nitrogen dioxide ( $\text{NO}_2$ ) through the sample, when a flocculent precipitate of elaidic acid (less soluble than the original oleic acid) will be produced. Nitrogen dioxide is best obtained by heating dry lead nitrate in a tube or small retort.

Fatty acids may be detected by diluting the glycerol with several times its bulk of water and acidifying with hydrochloric acid. In the presence of fatty acids the liquid becomes turbid.

By agitating glycerol with chloroform, fatty acids, rosin oil, and some other impurities are dissolved, while certain others form a turbid layer between the chloroform and the supernatant liquid. On separating the chloroform and evaporating it to dryness, a residue is obtained which may be further examined.

*o Lower fatty acids*, especially butyric and formic acids, may be not unfrequently present. The presence of free oxalic, formic, or butyric acid in distilled glycerol will be indicated by the acid reaction of the sample, and an estimate of the amount present can be obtained by titrating the diluted sample with standard alkali and litmus or phenolphthalein. *Butyric acid* is sometimes present to the extent of 0.5 per cent. of the fats saponified. Samples containing it develop an odor of sweat when mixed with a few drops of dilute sulphuric acid and rubbed between the hands. *Formic acid*, traces of which are often present

even in distilled glycerol, is best detected by adding ammonio silver nitrate to the diluted sample. On leaving the mixture at the ordinary temperature for half an hour, a black precipitate will be produced if formic acid be present. After a longer interval, all samples of commercial glycerol cause a reduction of ammonio silver nitrate, at least, if the liquid be exposed to light, and at temperatures above  $50^{\circ}\text{C}$  the change occurs with greater facility.

The presence of *formic* and *butyric acids* may be confirmed by gently heating the sample with alcohol and strong sulphuric acid, when esters of agreeable and characteristic odor will be formed. Ethyl formate has an odor of peaches, and ethyl butyrate that of pine-apple.

*p.* With a neutral solution of silver nitrate, pure diluted glycerol gives no precipitate. In presence of *formic acid*, *butyric acid*, or *acrolein*, a white precipitate is formed, which blackens on standing or boiling. French perfumers and manufacturers of cosmetics reject samples which show any change of color or turbidity within twenty-four hours after the addition of silver nitrate. Sulman and Berry find that nearly all commercial samples in bulk speedily effect reduction of the silver, with consequent blackening of the precipitate previously formed. *Nitric acid* has been found in distilled glycerol. Its presence, which cannot have been due to accident, masks the reaction with silver nitrate, and prevents the detection of impurities which are very objectionable in material intended for nitrating.

*q.* Distilled glycerol of good quality does not acquire a yellow or brown color when very gradually mixed with an equal measure of cold concentrated sulphuric acid. Sugar and certain other impurities cause a marked darkening, or even charring, and in presence of any considerable quantity of formic or oxalic acid the mixture effervesces when warmed. *Oxalic acid* may be recognised more certainly by the formation of a white turbidity on adding calcium acetate to the diluted sample. It is not unfrequently present in raw, but never in distilled samples.

*r.* Pure dilute glycerol does not sensibly reduce Fehling's copper solution when heated with the reagent to  $100^{\circ}\text{C}$ . for a few minutes, but prolonged boiling causes precipitation of the red cuprous oxide. *Glucose*, if present, will reduce the cupric solution even before the boiling point is reached. *Arsenious acid* will reduce Fehling's solution. Arsenic occurs in glycerin recovered from soap-lyes which have been neutralised by crude hydrochloric acid. *Cane sugar* can be recognised by the same test, if the sample be previously heated to  $70^{\circ}$  or  $80^{\circ}\text{C}$  for ten minutes in five times its measure of water and half its

measure of strong hydrochloric acid, and the inverted solution be neutralised with soda before adding the cupric solution. The test can be made quantitative if proper precautions be taken (see vol. 1. page 282 *et seq.*). Cane-sugar will be further indicated by the charring produced on mixing the sample with strong sulphuric acid, and warming, and glucose by the brown coloration produced on boiling the sample with a solution of caustic soda. Glucose may further be recognised by the reduction which ensues on heating the diluted glycerin to 70° C with potassium ferricyanide and caustic potash. On acidulating the solution and adding ferric chloride, prussian blue will be formed if glucose were originally present.

*s* Cane-sugar, glucose, and dextrin (but not milk sugar or arabin) may also be recognised by a test due to Mason. A mixture of 0.5 c.c. of the sample, 15 c.c. of water, 2 drops of strong nitric acid (not more), and 0.5 gm. of ammonium molybdate is boiled for two or three minutes, or longer if the quantity be small, when a blue coloration will be produced if 0.25 per cent. or more of either of the above impurities be present. Dextrin and gum would also be precipitated on diluting the sample with a large proportion of alcohol. They may be distinguished as described in vol. 1. page 426.

Sugar and other carbohydrates may also be detected and determined by observing the optical activity of the sample (see vol. 1). They can occur only as adulterants. Lajoux (*J. S. C. I.*, 1. 458) states that a saturated solution of magnesium sulphate mixed with glucose has been used in France as an adulterant for glycerol.

*t* The analysis of mixtures of sugar and glycerol has been already described (pages 288 and 289). If the actual separation of the two bodies for gravimetric determination or subsequent examination be desired, the best plan is to separate other organic bodies as far as possible by precipitating the cold solution with basic lead acetate used in slight excess (page 325), concentrate the filtrate at a low temperature, and extract the residue with a mixture of two measures of absolute alcohol and one of ether, or of two of alcohol and one of chloroform. These solvents leave the sugar undissolved, while the glycerol contained in the solution can be recovered more or less completely by evaporating the solution at a low temperature. If the solution be diluted with about twice its measure of water and faintly acidified before evaporating, the layer of ether or chloroform which separates often carries with it much of the coloring matter and resinous impurities which may be present, thus leaving the glycerol in a comparatively pure form.

u. The direct determination of *glycerol* in commercial samples can be effected imperfectly as above indicated, and more accurately as described on page 316 *et seq.*, in most cases, preferably by Hehner's dichromate method

Distilled glycerol can be distinguished from raw glycerin by the absence of any considerable proportion of fixed impurity (test c); and by its negative or faint reactions with basic lead acetate (test l) and calcium acetate (test q)

All so-called crude glycerin imported into the United States is examined by the government chemists to ascertain whether it is really crude or has been partially or wholly refined, as in the latter case a higher rate of duty is charged. Glycerin that has been freed from impurities by allowing them to subside and then straining and filtering, is still classed as "crude," but if proved to have been subjected to further purification it is classed as "refined." For practical purposes of classification distillation is regarded as the dividing line between crude and refined glycerin. For this purpose J. H. Wainwright (*J. A. C. S.*, 1889, 125) attaches great importance to the following tests —

The *Carbonaceous Residue* is obtained by heating 10 grm of the sample in a platinum crucible till it ignites, when the source of heat is removed and the sample is allowed to burn away spontaneously. In distilled glycerin this will not amount to 1 per cent. Crude glycerin may yield as much as 10 per cent. The percentage of ash appears to be a less reliable criterion.

*Silver Nitrate Test*—Five c.c. of the sample are diluted with 20 c.c. of distilled water, mixed with 5 c.c. of a 2 per cent solution of silver nitrate, and allowed to stand for one hour. Only a slight precipitate will be formed with distilled glycerin at the end of this time; whereas with crude glycerin the precipitate is large, usually comes down at once, and is almost always *flocculent*.

*Lead Test*—The solution is prepared by boiling 10 grm of lead acetate and 8 grm. of lead oxide with 500 c.c. of water, and filtering. Two volumes of this solution are mixed with one volume of glycerol and one of distilled water, and allowed to stand for an hour. Refined glycerin may produce a slight precipitate, but this is never *flocculent*. Crude samples produce a more or less abundant *flocculent* precipitate.

Wainwright does not consider it safe to rely upon either of the two last-mentioned tests alone, but if a sample will not stand both of them, it is thought perfectly safe to call it crude.

Glycerol intended for the manufacture of nitroglycerin must be free

from certain impurities, or dangerous results may ensue. It must be distilled and must further possess the following characters before it can be accepted as sufficiently pure —

1 Entire freedom from chlorides, iron, lead, and calcium (tests *e*, *f*, *h*)

2 Entire freedom from higher fatty acids (test *n*), and but feeble reaction with test *k*.

3 Entire freedom from sugar and other carbohydrates (tests *i*, *s*)

4 A specific gravity of not less than 1.260 at 15.5° C

According to Lewkowitsch (*Chem. Zeit.*, 1895, xix, page 1423) the glycerin used for the manufacture of nitroglycerin approaches in character chemically pure glycerol, having, however, a yellowish color, and containing a trace of ash and a small proportion of foreign organic bodies. Lead acetate must produce no precipitate. The specific gravity must be not below 1.261 at 15.5°. A low specific gravity associated with apparent high percentage of glycerol suggests the presence of trimethylene glycol, which has been found in some samples by Noyes and Watkins (*J. A. C. S.*, 1895, 890). Its presence in glycerin used for making nitroglycerin might be dangerous, since it reacts with nitric acid with explosive violence. Aluminum, calcium, and magnesium must be absent, and only traces of chlorine and arsenic are allowable. The quantitative estimation of the former is unnecessary, and for the latter a sample of the glycerin is made faintly alkaline with ammonium hydroxide, and silver nitrate added. No yellowish precipitate should be produced. Marsh's test for arsenic, and also Gutzeit's, even with mercuric chloride, are too delicate for the purpose. One c.c. of the sample, diluted with 2 c.c. of water, must remain almost unclouded. To test for other organic substances, a few drops of a 10 per cent silver nitrate solution are added to this solution. In ten minutes no browning or blackening must appear. The total residue may be determined as on page 326. It should not be more than 0.15 per cent. The basin is then ignited, the ash weighed, and the organic impurity calculated by difference. The sample must not redden litmus-paper. Volatile fatty acids, such as butyric, may be detected by the odor on heating with alcohol and strong sulphuric acid, and oleic acid by the flocks obtained on passing a current of nitrous anhydride through the sample.

It may often happen that a sample which will answer the above requirements is yet unsuitable for the manufacture of dynamite, it must, therefore, be nitrated in the following way, which imitates the conditions obtaining on the large scale. A mixture of one part by

weight of fuming nitric acid (sp gr 1.5) and two parts of pure sulphuric acid (1.845) is prepared, and allowed to cool in a stoppered vessel. 375 grm of the mixed acid are put into a thin-walled beaker of about 500 c.c capacity, and stood in a large vessel through which a constant current of cold water passes. Great care must be taken that the water does not splash into the beaker, to which end the leading tube should be firmly fixed both to the tap and the basin. 50 grm. of the glycerin are weighed out, and, when the acids are not hotter than from  $12^{\circ}$  to  $15^{\circ}$  C, added drop by drop, using a thermometer as a stirrer. The stirring must be very thorough to avoid local heating, and the temperature must not be allowed to exceed  $30^{\circ}$ ,  $25^{\circ}$  being a safer limit. The small beaker may be weighed again to give the exact amount of the sample added, and when the temperature of the other has fallen to  $15^{\circ}$ , the liquid is run out into a perfectly dry separating funnel, which may advantageously receive a preliminary rinse with strong sulphuric acid. The quicker the separation of the liquids, and the sharper the line of demarcation between the nitroglycerin and the acids, the better is the glycerin. The nitroglycerin is always slightly turbid, but if it contains flocks, or the separation be not complete in five or ten minutes, or if there be a cloudy middle layer of liquid, the glycerin must be rejected. With very bad samples, no separation at all may be obtained on standing several hours.

If it be desired to make the determination quantitative, the operation may be continued. The acids are run off, the nitroglycerin carefully swung round in the separator to detach drops of acid from the walls (without shaking it, however), and after these drops are removed, washed with warm ( $35^{\circ}$  to  $40^{\circ}$  C.) water, once or twice with 20 per cent soda, and again with water. It is then run into a 100 c.c burette, or graduated tube, and when the excess of water has risen to the top, the volume read off. This, multiplied by 1.6, gives its weight, and the yield should be at least from 207 to 210 per cent, —the higher the better (theory requires 246.7 per cent). If preferred, it may be weighed directly after filtration over salt, and its specific gravity taken. The loss in the wash-waters is insignificant.

To destroy the nitroglycerin, it is best absorbed in a thin layer of sawdust spread in an open yard removed from any buildings, and then set on fire with a match. It will burn away quietly.

Glycerol intended for pharmaceutical or medical use should be distilled. An article answering to the tests of the British Pharmacopoeia has a specific gravity of about 1.25, and is free from chlorides, sulphates, calcium, heavy metals, and acid or alkaline reaction. When

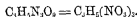
gently heated with dilute sulphuric acid no rancid odor is produced, and when shaken with an equal measure of strong sulphuric acid no coloration, or only a very slight straw coloration, results. The United States Pharmacopœia further directs that the glycerol should not give a decided precipitate of cuprous oxide when heated to 85° C with Fehling's solution, either with or without being previously boiled for half an hour with dilute hydrochloric acid. No sensible amount of carbonaceous residue should be left on burning away 2 gm. of the sample, and no ash after complete ignition. For medical use it should, of course, be free from appreciable amounts of arsenic.

*Arsenic* may often be detected by Reinsch's test, but Gutzzeit's test is more delicate. It is performed as follows:—

Place in a tall test-tube about a gram of pure zinc, 5 c.c. of diluted sulphuric acid (6 per cent), and 1 c.c. of the sample. The mouth of the test-tube is then covered with a tightly fitting cap, made of three thicknesses of filter-paper. A drop of strong solution of silver nitrate is placed on the upper layer and the tube allowed to stand for ten minutes in the dark. If arsenic be present, a bright yellow stain will appear on the filter-paper, which, on the addition of water, becomes black or brown. A blank test should always be made to establish the absence of arsenic in the reagents. Sulphides (which may be detected by substituting lead acetate for the silver nitrate in the above test) must be oxidised to sulphates before applying the test.

The test is extremely sensitive. A less rigorous test may be made by substituting a drop of a saturated solution of mercuric chloride for the silver nitrate. If no yellow coloration appears after ten minutes, the sample may be considered free from arsenic.

#### **Trityl Nitrate. Nitroglycerin.**



When strong glycerol is gradually added to a well-cooled mixture of very strong nitric and sulphuric acids, it is converted into trityl nitrate, or nitroglycerin, formerly called "glonoin oil." When great care is taken, nearly the theoretical yield is obtainable; but if the temperature be allowed to rise, a more complex reaction ensues, with formation of oxalic acid, glyceric acid, etc., and if the action be very violent, spontaneous explosion may take place. This may also occur if the glycerol be impure.

Nitroglycerin is a heavy oily liquid, of 1.600 specific gravity at

15° C When pure it is colorless, but the commercial product has a yellow color. It solidifies at about 8° C According to Lobry de Bruyn ebullition does not take place at 160° C even under a pressure of 15 mm.

Nitroglycerin has no marked odor, but is sensibly volatile at ordinary temperatures, and the vapor causes a violent headache in those unaccustomed to it, but most of those employed in handling dynamite do not suffer from the effects It is employed in medicine, and is poisonous even in small doses It is not readily inflammable, and when ignited commonly burns with a greenish flame, without explosion.

Its most characteristic property, and that which has the most important application, is its high explosive force. It explodes with violence when smartly struck or compressed, or when dropped on an iron plate heated to 257° Absorbed by sawdust, *Lieselguhr* (infusorial earth), or other inert porous material, it produces the varieties of dynamite, and combined with gun-cotton it constitutes "blasting gelatin" Nitroglycerin is miscible in all proportions with ether, chloroform, glacial acetic acid, and phenol, and is also very soluble in benzene, but it dissolves only sparingly in glycerol, carbon disulphide, or amyl alcohol It is slightly soluble in water (1 gm in 800 cc), but dissolves in alcohol, and more readily in wood spirit, and is precipitated from these solutions on addition of water This fact may be used for its purification, and by subsequently titrating the aqueous liquid with standard alkali for ascertaining the proportion of free acid in the commercial product and its preparations. The presence of free acid indicates imperfect manufacture, and a special liability to spontaneous decomposition and explosion. Nitroglycerin is easily saponified by alcoholic potash, and is reduced by various deoxidising agents. Its reactions are described more fully on next page.

#### DETECTION OF NITROGLYCERIN.

For the recognition of nitroglycerin it is usually necessary to isolate it in a state of approximate purity This may be generally done by extracting it by ether or benzene and evaporating the solution; or by dissolving in alcohol or wood spirit and precipitating the nitroglycerin by diluting the solvent with water

When isolated, nitroglycerin may be recognised by its physical characters, and the following methods —

- 1 A drop of the liquid allowed to spread on filter paper burns quietly with a peculiar greenish flame on igniting the paper.

- 2 A drop of the liquid placed between two folds of non-absorbent



paper explodes violently when smartly struck with a hammer on an anvil. The experiment may fail unless a violent blow be given which catches the drop fairly.

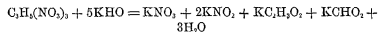
3 A drop of the liquid allowed to fall on an iron plate heated to about  $257^{\circ}\text{C}$  explodes violently. If this temperature be much exceeded the liquid inflames without detonating, and at a lower temperature it evaporates without igniting.

4 If dissolved in alcohol, and warmed with ammonium sulphide, nitroglycerin is decomposed, ammonium nitrite, glycerol and free sulphur being produced. If excess of sulphide be removed by zinc sulphate, and the liquid filtered, the nitrite may be detected by the usual tests.

5 A drop of nitroglycerin, when treated with a solution of ferrous sulphate acidulated with hydrochloric acid, gives the brown coloration characteristic of nitrates and nitrites.

#### DETERMINATION OF NITROGLYCERIN.

1 When boiled with alcoholic potash, nitroglycerin is readily saponified, but the products are not simply glycerol and potassium nitrate, a more complicated reaction takes place. According to M. Hay no glycerol is obtained, as it is oxidised at the expense of the  $\text{NO}_2$  groups, about two-thirds of which suffer reduction to the nitrous condition, only about one-third being found as nitrate. The principal reaction appears to be as follows.—



Besides the nitrate, nitrite, acetate, and formate shown in this equation, some oxalate is formed, together with a small amount of ammonia, and a reddish brown resinous substance, probably aldehyde-resin, which gives a dark color to the liquid. This reaction appears to occur in a fairly definite manner. Thus, Hay found the proportion of nitrous anhydride ( $\text{N}_2\text{O}_4$ ) produced by the saponification of 100 parts of nitroglycerin to range between 34.14 and 35.24, the theoretical yield corresponding to the above equation being 33.48. The author has attempted to apply Koettstorfer's principle (page 53) to the assay of nitroglycerin, but though the results obtained were fairly concordant, the dark color of the liquid prevented the point of neutrality from being ascertained with accuracy by any of the indicators tried.

2 Champion and Pellet adopt the following method of determining the  $\text{NO}_2$  of nitroglycerin. A known quantity of solution of ferrous

sulphate of previously ascertained reducing power is placed in a flask, acidified strongly with hydrochloric acid, and its surface covered with a layer of petroleum oil. About 0.5 grm. of the nitroglycerin is then introduced, and the flask heated on a water-bath. When the sample is completely decomposed the liquid is heated to boiling to remove nitric oxide, and the excess of ferrous sulphate ascertained by titration with standard permanganate. Fifty-six parts of iron, oxidised by the sample correspond to 20.67 of  $\text{NO}$ , in the nitroglycerin, or to 25.2 parts of tritenyl nitrate.

3. Instead of calculating the nitroglycerin from the amount of iron oxidised, it may be deduced from the volume of nitric oxide gas evolved in the reaction. For this purpose a modification of Eykman's method of assaying spirit of nitrous ether may be advantageously employed. The apparatus and method of manipulation are described in volume 1 page 200 *et seq.* About 5 grm. of ammonium ferrous sulphate and 50 c.c. of water should be introduced into the flask, and, when all the air has been expelled by boiling the liquid, and the apparatus has become quite cool, a solution of about 0.1 grm. of nitroglycerin in about 5 c.c. of concentrated sulphuric acid is introduced, taking care to allow no air to enter. This is followed by about 50 c.c. of a mixture of equal measures of strong sulphuric and hydrochloric acids. The contents of the flask are then boiled till the evolution of gas is complete, when the nitric oxide evolved is measured, with due precautions, in the usual way. The number of centimetres of gas obtained, at  $0^\circ \text{C}$  and 760 mm pressure, multiplied by 0.6269, gives the nitrogen in milligrams, or, multiplied by 3.39, gives the corresponding weight of tritenyl nitrate.

4. Instead of operating in the foregoing manner, Hempel and Lunge determine the nitric oxide evolved by agitating the sample with sulphuric acid over mercury, under which conditions nitroglycerin behaves like an ordinary nitrate. An accurately weighed quantity, varying from 0.12 to 0.35 grm., according to the proportion of nitroglycerin and the capacity of the apparatus, is introduced into the cup of a nitrometer filled with mercury. About 2 c.c. of concentrated sulphuric acid is then added, and when the nitroglycerin is dissolved the solution is allowed to enter the nitrometer through the tap. The cup is rinsed with successive portions of 2 c.c. and 1 c.c. of strong sulphuric acid, which are allowed to enter as before, and the contents of the nitrometer are then thoroughly agitated in the usual way, and the volume of nitric oxide evolved read off after standing about fifteen minutes. As stated above, the volume of gas in c.c. at the standard

pressure and temperature, multiplied by 3.39, gives the weight of nitroglycerin in milligrams. Hempel states that the total volume of 5 c.c. of sulphuric acid must not be departed from, with less than that volume the reaction proceeds too slowly, and with more the results are too low.

#### ANALYSIS OF DYNAMITE, &c.

Nitroglycerin is the leading ingredient of a number of explosive mixtures, called by a variety of fanciful names, and which are sometimes of a very complex composition. Among the explosive constituents of these mixtures are nitroglycerin, gun-cotton, collodion cotton, and nitrated wood, the absorbent materials include kieselguhr (infusorial earth), sandarite, tripoli, clay, alumina, sawdust, wood, charcoal, coal, lignite, &c., some of which are also combustible, as are resin, camphor, paraffin, and sulphur, among the oxygenating bodies are potassium, sodium, and barium nitrates; while sodium, ammonium, calcium, and magnesium carbonates are added as antacids (see table, p. 338).

In assaying nitroglycerin preparations it is necessary to determine the *water* by drying the finely-divided substance (which should be cut up or crushed with a horn spatula or ivory paper-knife) in a vacuum over sulphuric acid, as nitroglycerin volatilises sensibly with the least increase of temperature.

Ordinary dynamite—which usually contains 75 per cent. of nitroglycerin absorbed by 25 per cent. of ignited infusorial earth, to which a small proportion of alkali-carbonate has been added as an antacid—may be conveniently examined by exhausting the dried sample with anhydrous ether, preferably in a Soxhlet-tube, and weighing the insoluble residue. The nitroglycerin is estimated from the loss, and in the absence of other substances soluble in ether, such as camphor and resin, this is the most satisfactory way. Many operators evaporate the ethereal layer and weigh the residual nitroglycerin, but the author has found this method faulty, as it is almost impossible to prevent loss of nitroglycerin, even when the ethereal solution is allowed to evaporate spontaneously at the ordinary temperature.

In the absence of metallic nitrates and of the different varieties of nitrocellulose which are present in blasting gelatin, nitroglycerin may be at once determined by one of the methods described on page 335, but otherwise it must be previously isolated by treating the mixture with ether. Even the best of these methods only estimate the  $\text{NO}_2$ , and hence do not actually determine the nitroglycerin present, which is not always strictly trinitrophenyl nitrate, besides which dynamite contains

traces of metallic nitrates. The determination of nitroglycerin by difference is usually the most satisfactory

COMPOSITION OF SOME WELL-KNOWN NITROGLYCERIN EXPLOSIVES

NAME	PER- CENT- AGE OF NITRO- GLYC- ERIN	OTHER INGREDIENTS
<b>DYNAMITES</b>		
Kieselguhr Dynamite (Giant Powder, No 1)	75	Kieselguhr, 21.5, and carb. 0.5
" " " " (No 2)	40	Sodium nitrate, 40, sulphur, 6, resin, 8, Kieselguhr, 8
Rhexite of Carl Diller, "	64	Sodium nitrate, 18, decayed wood, 11, wood meal, 7
Megamite of Schuckher & Co., "	60	Nitrated wood, 10, nitrated vegetable ivory 10, sodium nitrate, 20
Dynamite of Vonges, France, "	75	Decomposed feldspar, 20.8, quartz, 3.8, magnesium carbonate, 0.4
Carbonite, Schmidt & Bichel, "	25	Wood meal, 40.5, sodium nitrate, 44, sodium carbonate, 0.5
Stonite " " "	68	Kieselguhr, 20, wood-meal, 4, potassium nitrate, 8
Hercules Powder, "	40	Sodium nitrate, 45, wood pulp, 11, sodium chloride, 1, magnesium carbonate, 1, moisture, 2
Vulcan Powder, "	30	Sodium nitrate, 52.5, sulphur, 7, charcoal, 10.5
Safety Nitro-Powder "	68.81	Sodium nitrate, 18.35, wood-pulp, 12.84
Judson Powder, " " "	5	Sodium nitrate, 64, sulphur, 16, cannel coal, 16
Atlas Powder, " " "	75	Sodium nitrate, 2, wood-fibre, 21, magnesium carbonate, 2
Vigorite, " "	30	Potassium chlorate, 40, potassium nitrate, 7, wood pulp, 9, magnesium carbonate and moisture, 7
Pulverulent Ammonium Dynamite,	20	Ammonium nitrate, 25, sodium nitrate, 36, roasted rye-flour, 36
Dynamite No 3, for giant mines,	15	85 of absorbent powder, consisting of sodium nitrate, coal, and sodium carbonate
Carbo-Dynamite of Reed & Berland,	90	Cork-charcoal 10
CORDITE,	58	Gun-cotton, 37, vaseline, 7
BALLISTITE,	60	Collodion-cotton, 40, aniline, 1
BLASTING GELATINE,	90-96	Soluble gun-cotton, 4-8 Camphor sometimes added
GELATINE DYNAMITE,	40	Nitro-cotton, 1, sodium nitrate, 38, tar, sulphur, and wood-pulp

The following systematic scheme for the analysis of nitroglycerin preparations is a modification of the methods proposed by F. Hess, G. Lunge, Champion and Pellet, and others.—

# OUTLINE SCHEME FOR THE ANALYSIS OF NITROGLYCERIN PREPARATIONS

Exhaust the previously dried substance with anhydrous ether, preferably in a Soxhlet-tube

SOLUTION —Divide into two equal parts		RESIDUE —Dry, weigh, and exhaust with water, preferably in the Soxhlet-tube.	
<p>A.—Allow the ether to evaporate spontaneously dry the residue, and add excess of 300 cc. anhydrous ether, shake with water, shake with ether, and separate</p> <p>Weight given as residue</p> <p>WATER-SOLUBLE RESIDUE</p> <p>glycerol, resin, camphor, (isophthalic acid, and paraffin). Determine water by method 2 or 3, page 335</p>	<p>B.—Add phenolphthalein and titrate with alcoholic potash i.e. of normal potassium hydroxide solution. Add 100 cc. of 95% alcohol, shake with water, shake with ether, and separate</p>	<p>SOLUTION contains metallic nitrate, chlorides, soluble carbonates, and other salts which (exclusive of ammonium carbonate) can be determined by evaporating the solution to dryness, and weighing the residue. The nitrate can be conveniently determined by the nitrometer</p>	
	<p>ETHER-INSOLUBLE RESIDUE</p> <p>—Add benzene, and shake with by dichloric acid, and separate. Add 100 cc. of 95% alcohol, shake with water, shake with ether, and separate</p> <p>Weight given as residue</p> <p>WATER-SOLUBLE RESIDUE</p> <p>glycerol, resin, camphor, (isophthalic acid, and paraffin). Determine water by method 2 or 3, page 335</p>	<p>SOLUTION —Evaporate to dryness, and weigh the residue. The nitrate can be conveniently determined by the nitrometer</p>	<p>RESIDUE —Dry, weigh, and treat a weighed portion in nitromethane, and extract with ether. If present, extract with ether. If present, extract with ether. If present, extract with ether.</p>
		<p>RESIDUE —Dry, weigh, and treat a weighed portion in nitromethane, and extract with ether. If present, extract with ether. If present, extract with ether.</p>	<p>RESIDUE —Dry, weigh, and treat a weighed portion in nitromethane, and extract with ether. If present, extract with ether. If present, extract with ether.</p>

1. The sample is determined by difference

2. As sulphur is only very sparingly soluble in ether, it is preferable to extract some of the original substance with water and treat the residue with alcoholic potash, add bromine, acetic acid, and precipitate as barium sulphate.

**Heating Test for Nitro-explosives** —The following test prescribed by the British Home Office has been very generally adopted in order to determine the extent to which an explosive is liable to decompose during storage —

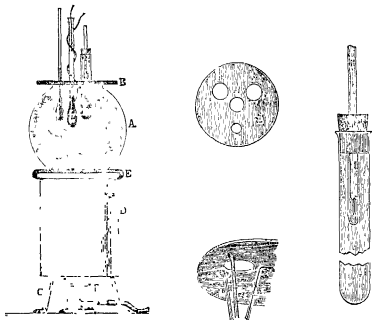


FIG 12

### Apparatus required

1. A water bath, consisting of a spherical glass or copper vessel (A) of about 8 inches in diameter, with an aperture of about 5 inches, it is filled with water to within a quarter of an inch of the edge. It has a loose cover of sheet-copper about 6 inches in diameter (B) and rests on a tripod-stand about 14 inches high (C), which is covered with coarse iron wire gauze (E), surrounded with a screen of thin sheet-iron or copper (D). Within the latter is an argand lamp (F) with glass chimney. The cover (B) has four holes, arranged as seen in the figure. Nos 1 and 2, the test-tubes containing the material to be tested, No 3, the thermometer, No. 4, to receive the regulator. Around holes 1 and 2 on the under side of the cover are soldered three pieces of brass wire with points slightly converging, these act as

springs, and allow the test tubes to be easily placed in position and removed

2. *Scheibler's or Puge's temperature regulator*

3 *Two cells of Leclanché's battery, No. 1* } if Scheibler's regulator be

4 *A few yards of insulated copper wire* } used

This regulating apparatus is not essential, as the temperature of the bath can be kept constant by proper attention to the heating flame

5 *Test-tubes* from 12 to 14 cm long, and of such a diameter that they will hold 20 to 22 c c. of water when filled to a height of 12.5 cm.

6 *India-rubber stoppers*, fitting the test-tubes and carrying an arrangement for holding the test papers, viz., a narrow glass tube passing through the centre of the stopper, drawn out so as to form a hook, or terminating in a platinum-wire hook

7 *A thermometer* with range at least from 0 to 100° C.

8 *A minute clock*

#### Materials required:

(a) *Test paper*, prepared as follows.—3 gm of white maize starch (corn-flour) previously washed with cold water, are added to 250 c.c. of distilled water, the mixture stirred, heated to boiling, and kept gently boiling for ten minutes, 1 gm of pure potassium iodide (i.e., which has been recrystallised from alcohol) are dissolved in 250 c c of distilled water. The two solutions are thoroughly mixed and allowed to get cold. Strips or sheets of white English filter-paper, previously washed with water and dried, are dipped into the solution thus prepared, and allowed to remain in it for not less than ten seconds, they are then allowed to drain and dry in a place free from laboratory fumes and dust. The upper and lower margins of the strips or sheets are cut off and the paper is preserved in well-stoppered or corked bottles *in the dark*. The freshly-prepared paper, and that which is still in good condition, will give no coloration when a drop of dilute acetic acid is put on it. In time, however, and soonest in a strong light a drop of the acid produces a brown or bluish coloration. A single hour of direct sunlight produces a marked effect. When this change occurs the paper is spoiled. On this account it is advisable to prepare but little of the test paper at one time, and not to use any that is more than one month old. The dimensions of the pieces of test-paper used are about 10 by 20 mm

(b) *Standard Tint-paper*—A watery solution of caramel is made of such strength that when diluted 100 times the tint of the solution

equals that produced by Nessler reagent in 100 c.c. of water containing 0.00023505 grm. of ammonium chloride. With this caramel solution lines are drawn by means of a clean quill-pen on strips of white filter-paper previously washed with distilled water to remove traces of bleaching matter, and dried. When these marks are dry, the paper is cut into pieces of the same size as the test paper previously described, so that each piece has a brown line across it near the middle of its length. Only those strips are used in which the brown line has a breadth varying from .5 to 1 mm.

A. *Nitroglycerin preparations*, from which the nitroglycerin can be extracted in the manner described below, must satisfy the following test, otherwise they will not be considered as manufactured with "thoroughly purified nitroglycerin" within the terms of the license. The test, however, is only one of several which the preparation will have to satisfy in order to establish its compliance with the definition.

*Separation of the Nitroglycerin*—About 20 to 25 grm. of dynamite finely divided are placed in a funnel loosely plugged with some finely-ignited asbestos. The surface is smoothed by means of a flat-headed glass rod or stopper, and some clean-washed and dried diatomaceous earth is spread over it to the depth of about one-eighth of an inch. Water is next carefully dropped upon the mass from a wash-bottle, and when the first portion has been soaked up more is added; this is repeated until sufficient nitroglycerin has been collected in a graduated vessel placed below.

If any water should have passed through with the nitroglycerin, it should be removed with a piece of blotting-paper, and the nitroglycerin filtered, if necessary, through a dry paper filter.

*Application of the Test*—The thermometer is inserted through the lid of the water bath described above, into the water (which is to be steadily maintained at a temperature of 160° F. (71° C.) to a depth of 7 cm. 3.24 grm. (50 grains) of the nitroglycerin to be tested are weighed into a test-tube in such a way as not to soil the sides of the tube. A test-paper is fixed on the hook of the glass rod, so that when inserted into the tube it will be in a vertical position. A sufficient amount of a mixture of half distilled water and half glycerol to moisten the upper half of the paper is now applied to the upper edge of the test paper, by means of a camel's-hair pencil; the cork carrying the rod and paper is fixed into the test-tube, and the position of the paper adjusted so that its lower edge is about half-way down the tube; the latter is then inserted through one of the perforations of the cover to such a depth that the lower margin of the moist-



ened part of the paper is about 16 cm above the surface of the cover. The test is complete when a faint brown line, which after a time makes its appearance at the line of boundary between the dry and moist part of the paper, equals in tint the brown line of the standard tint-paper.

The nitroglycerin will not be considered as "thoroughly purified" within the terms of the license unless the time necessary to produce the standard tint as above described is *at least* fifteen minutes. In laboratories where many tests are made daily, the nitroglycerin is not weighed, but is measured by a pipette holding about the quantity mentioned above when filled to the mark. The test-papers must never be touched with the hands, since they are influenced by the least impurity. It is advisable to have a large piece of cork in readiness on which the test-paper is put from the bottle by means of a pair of pincers and held there with them, whilst with a second pair of pincers a hole is first made in the paper and the glass hook inserted in the hole. The glycerol solution can then be put on the paper by means of a glass rod; as a rule, a small drop is sufficient for the purpose.

In the laboratory of the U S Military School at Ft Monroe, Va., 0.324 grm. (5 grains) are used for the test, and the time allowed for the appearance of the color is ten minutes. (See "Lectures on Explosives," by Lieut W Walke)

B *Blasting gelatine, gelatine dynamite*, and analogous preparations. 3.24 grm of blasting gelatine are intimately incorporated with double its weight of French chalk (this can be readily effected by carefully working the two materials together with a wooden pestle in a wooden mortar). The mixture is to be gradually introduced into a test tube of the dimensions prescribed above for the dynamite test, with the aid of gentle tapping on the table, between the introduction of successive portions of the mixture into the tube, so that when the tube contains all of the mixture it shall be filled to the extent of 4.5 centimetres of its height. The test-paper is then to be inserted and heat applied in the manner prescribed above for the dynamite heat-test, and the sample tested is to withstand exposure to 160° F (71° C) for a period of ten minutes before producing a discoloration of the test-papers corresponding in tint to the standard color-test which is employed for governing the results of the dynamite heat-test.

C *Cordite and Similar Smokeless Powders*.—From each end of each piece of cordite selected for the test, pieces of 1 inch length are cut. With thicker cordite each piece is further cut into about four parts. With flake or cube powder a division is made in a similar manner.

The pieces are passed two or three times through a pug-mill, and the part first passing is put aside, as it may contain foreign substances from the mill. The ground material is passed through a set of three sieves. That which has passed through the coarsest sieve and is retained by the second one is used for the test. After each grinding the mill must be taken apart and thoroughly cleaned.

For the test, 1.62 gm. of cordite are put, with light shaking, into a test-tube, which is provided with a test-paper moistened with glycerol as described above. The water in the bath is kept at a temperature of  $82.2^{\circ}\text{C}$ . The lower end of the moistened part of the paper should be about 15.6 mm. above the surface of the cover of the bath. The brown line on the test-paper must not appear in less than fifteen minutes.

D. *Gun cotton, Schultze Powder, E. C. Powder, and Similar Explosives*—Sufficient material to serve for two or more tests is removed from the center of the cartridge by gentle scraping, and, if necessary, further reduced by rubbing between the fingers. The fine powder thus produced is spread out in a thin layer upon a paper tray, 11 by 15 cm., which is then placed in a water-oven, kept, as nearly as possible, at  $49^{\circ}\text{C}$ . The oven should have wire-gauze shelves about 7.5 cm. apart. The sample is allowed to remain for fifteen minutes, the door being left wide open. The tray is then removed and exposed to the air of the room for two hours. The powder should be rubbed upon the tray with the hand, in order to reduce it to a fine and uniform state of division.

*Application of the Test*—The cover of the water bath is fitted with the gas regulator, which is inserted through the centre hole (No. 4). The thermometer is fixed in hole No. 3. The water is heated to  $66^{\circ}\text{C}$ ., and the regulator set to maintain that temperature. 1.296 gm. (20 grs.) of the sample are placed in the test-tube of the dimensions specified, and gently pressed down until it occupies a space of (as nearly as possible) 3.12 cm. A test-paper is affixed to the hook of the glass rod, and moistened by touching the upper edge with a drop of distilled water containing 50 per cent of pure glycerol. The quantity of liquid used must be only sufficient to moisten about half of the paper. The cork carrying the rod and test-paper is then fixed in the test-tube and the latter inserted into the bath to a depth of 6.25 cm. measured from the cover, the regulator and thermometer being inserted to the same depth. The test-paper is to be kept near the top of the test-tube, but clear of the cork, until the tube has been immersed for about five minutes. A ring of moisture will, in about this time, be deposited upon the sides of the test-tube, a little above the cover of the bath,

the glass rod must then be lowered until the lower margin of the moistened part of the paper is on a level with the bottom of the ring of moisture in the tube, the paper is now closely watched. The test is complete when a very faint brown coloration makes its appearance at the line of boundary between the dry and moist parts of the paper.

The time interval between the first insertion of the tube containing the sample of gun-cotton in the water at 66° C. and the first appearance of discoloration on the paper must not be less than ten minutes.

#### Exudation and Liquefaction Tests for Blasting Gelatine, Gelatine Dynamite, and Analogous Preparations.

*Tests for Liquefaction*—A cylinder of blasting gelatine should be cut from the cartridge to be tested and be placed on end on a flat surface without any wrapper, and secured by a pin passing vertically through its centre. The length of the cylinder should be about equal to its diameter and the ends cut flat. The cylinder is to be exposed for one hundred and forty-four (144) consecutive hours (six days and nights) to a temperature ranging from 30° to 32° C inclusive, and during such exposure the cylinder shall not diminish by more than one-fourth of its original height, and the upper cut surface shall retain its flatness and the sharpness of its edge.

If the blasting gelatine and gelatine dynamite be not in cylindrical form, the test must be modified accordingly.

**LIMIT OF LIABILITY TO EXUDATION.**—The general mass of a blasting gelatine or gelatine dynamite should not allow of the separation under any conditions of storage transport, or use, of a substance of less consistency than the bulk of the remaining portion, nor when the material is subjected three times in succession to alternate freezing and thawing, nor when subjected to the above liquefaction test.

#### Diphenylamine Heat Test.

Guttmann (*J.S.C.I.*, 1897, 283) states that the official heat-test as given above is inapplicable to most smokeless powders, and to some blasting explosives, since the iodine supposed to be liberated, is acted upon by some of the ingredients—*e.g.*, castor oil, acetone, and vaseline. After examination of a number of methods for the detection of nitrogen dioxide he advises the diphenylamine test—

One gram of diphenylamine is placed in a wide-necked flask provided with a ground stopper, 50 c.c. of dilute sulphuric acid (10 c.c. of concentrated sulphuric acid to 40 c.c. of water) added, and the flask heated in a water-bath to between 50° and 55° C until the solution is

effected. The flask is removed, well shaken, and allowed to cool. After cooling, add 50 c.c of pure glycerol, shake well, and preserve the solution in the dark. The test is applied as follows. The explosive is finely divided as directed in the Home Office regulations, smokeless powder being ground in a bell-shape coffee-mill and sifted. 1.5 gm (from the second sieve in the case of smokeless powder) are placed in a test-tube. Strips of well-washed filter-paper, 25 by 10 mm, are to be hung on a hooked glass rod as usual. The diphenylamine solution is taken up by means of a clean glass rod, and a drop placed on each of the upper corners of the filter-paper, so that when the two drops run together about a quarter of the filter-paper is moist. The paper is then put into the test-tube, which is placed in the water-bath, heated to 70° C. The reaction should appear in less than fifteen minutes. It will begin by the moist part of the paper becoming a greenish-yellow, and from this moment the paper should be carefully watched. After one or two minutes a dark-blue mark will suddenly appear on the dividing line, between the wet and dry portion; the time required for this appearance is to be noted.

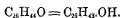
The following table shows some of the results obtained:—

HEAT TESTS OF VARIOUS SMOKELESS POWDERS. TEMPERATURE, 80° C  
QUANTITY OF POWDER, 1.5 GRM

NAME.	COMPOSITION.	TIME IN MINUTES.	
		Iodine Paper	Diphenylamine Paper
Spotting ballistite,	Nitroglycerin and nitrocellulose, no solvent	13	13
Hobson Maxam's powder,	Nitroglycerin and gun-cotton	60	9
Hobson Maxam's "	Nitroglycerin and gun-cotton, with 2 per cent ester oil	120	11
Gunn's cotton, "		9	8½
Schultze,	Wood-nitrocellulose and potassium nitrate	16	14
Explosive Company, oxygen 1,	Nitrocellulose, potassium nitrate	10	11
" " " No 1,	" " " "	4	5
" " " No 2,	" " " " camphor	25	Not tested
" " " No 3,	" " " "	76	No trace
Wibrodte, Ki,	Nitrocellulose dissolved in acetic ether	67	22
" " P. P.	" " " " "	50	20
" " W. G. P. 92-A,	" " " " "	59	21
" " B. G. P. 92,	" " " " "	15	17
" " K. P. 2,	" " " " "	50	26
" " Cannon,	" " " " "	75	No trace
von Forster, Spotting,	Nitrocellulose—solvent, acetone	19	6
" " Rifl., No 2,	" " " "	20	14
" " " No 3,	" " " "	80	No trace

## CHOLESTEROL.

## Cholesteryl Alcohol.



Cholesterol is a substance which occurs very frequently, both as an animal and a vegetable product. It is present in the brain, yolk of eggs, perspiration and the liquid of ovarian tumors. It is a product especially characteristic of the liver,—biliary calculi being sometimes almost wholly composed of it. In shark-liver oil the author has found it in considerable quantity, and has also isolated it from cod-liver oil, butter fat, &c. It occurs in olive oil, but it exists in considerable proportion in the fatty matter of sheep's wool.

Cholesterol is deposited from its solution in chloroform in anhydrous needles, having a specific gravity of 1.067. It is tasteless and odorless. It melts at 147° C., and if carefully heated may be sublimed unchanged at a higher temperature. When subjected to dry distillation it yields a carbonaceous residue and a neutral oil insoluble in potassium hydroxide, from which a second distillation with water separates a volatile oil having an agreeable odor of geranium.

Cholesterol is quite insoluble in water, even when boiling. It is sparingly soluble in cold alcohol, but readily in the boiling liquid, and is easily dissolved by methyl alcohol, ether, chloroform, carbon disulphide, benzene, turpentine, and petroleum spirit. It is also soluble in fixed oils, purified bile, and solutions of soap.

The alcoholic solution of cholesterol is neutral in reaction. It is levorotatory, the specific rotation for the sodium ray being —36.6°, according to Dragendorff, or —31.6° according to Lindenmeyer.

Cholesterol is deposited on gradually cooling its hot alcoholic solution in crystals containing 1 molecule of water. The crystals are nacreous laminae, of a highly characteristic appearance.

Cholesterol is unacted on by dilute acids or concentrated alkaline solutions, but is decomposed when fused with caustic potash. Lewkowitsch has noted that when cholesterol is heated with soda-lime, no, or at most very small quantities of, fatty acids are formed—an important difference from aliphatic alcohols.

If anhydrous cholesterol be dissolved in carbon disulphide, and a dilute solution of bromine in the same menstruum gradually added, a cholesterol dibromide,  $C_{26}H_{44}O.Br_2$ , is obtained. This body crystallises in small colorless needles, melts at 147°, and is reconverted into cholesterol by the action of nascent hydrogen.

The calculated iodine-absorption of cholesterol is 68.3. Lewkowitsch obtained figures closely approximating to this.

By oxidation with chromic acid mixture, cholesterol is converted into a white amorphous acid, having the composition of oxycholeic acid,  $C_{25}H_{40}O_6$ , small quantities of acids of the acetic series being also produced.

#### CHOLESTERYL ESTERS

In its chemical relationships, cholesterol behaves as a monatomic alcohol. On adding sodium to its solution in purified petroleum, sodium cholesterylolate,  $C_{27}H_{46}NaO$ , is formed with evolution of hydrogen. By the action of phosphorus pentachloride, or by heating it with concentrated hydrochloric acid, cholesteryl chloride,  $C_{27}H_{45}Cl$ , is obtained as a crystalline substance melting at  $100^\circ$ . Cholesterol also reacts with organic acids to form a series of ethereal salts, of which the acetate and benzoate are the most interesting.

*Cholesteryl Acetate*,  $C_{29}H_{48}C_2H_3O_2$ , is formed by the action of acetyl chloride on sodium cholesterylolate, or of acetic anhydride on cholesterol (see pages 353 and 354). It crystallises in small, colorless needles, which melt at  $92^\circ$ , and are nearly insoluble in cold and with difficulty in boiling alcohol, but are soluble in ether.

*Cholesteryl Benzoate*,  $C_{29}H_{48}C_7H_5O_2$ , is obtained by heating cholesterol with benzoic acid under pressure (page 353). It crystallises from ether in small glistening rectangular tablets, melting at  $150$ – $151^\circ$  C.

On treating the various cholesteryl esters with alcoholic potash, they readily undergo saponification, and, after evaporating off the alcohol and treating the residue with water, the cholesterol can be extracted from the aqueous liquid by agitating it with ether.

#### Detection of Cholesterol.

When existing in a moderately pure state, cholesterol is easily recognised by its highly characteristic crystalline form. The substance to be tested should be boiled with alcohol, the solution filtered while hot, and allowed to cool slowly. Either immediately on cooling or after previous concentration, the cholesterol will be deposited in crystals, which, viewed under a moderate microscopic power, with a diaphragm having a small aperture, appear as thin, very transparent rhombic plates, the angles of which are extremely well defined, and constantly measure  $79^\circ 30'$  and  $100^\circ 30'$ .

The formation of the characteristic acetate and benzoate, with deter-

minations of the melting points of these esters, will sometimes afford valuable means of identifying cholesterol, as also of isolating it from other bodies (pages 353 and 354)

Cholesterol gives a number of well-marked color-reactions, of which the following are the chief —

If a crystal be treated with a mixture of 5 volumes of concentrated sulphuric acid and 1 volume of water, and the whole gently heated and examined under the microscope, it is seen to have become a fine carmine-red color at the edges, and after an hour or two the red tint changes to violet. With a mixture of 3 measures of acid to 1 of water, a violet coloration results, and with more dilute acid the edges appear of a lilac color

If cholesterol be titrated with a little concentrated sulphuric acid, and chloroform added, a blood-red solution is produced, which, on exposure to air, becomes successively violet, blue, green, and ultimately colorless

To obtain the last reaction, Salkowski proceeds in the following manner — About 10 milligrams of cholesterol are dissolved in 2 c c of chloroform, and the solution shaken with an equal measure of sulphuric acid of 1.76 sp gr. The chloroform layer immediately becomes colored, passing from blood-red to cherry-red and purple, which last tint it retains for several days. A cautious addition of fuming nitric acid to the mixture causes these changes to occur rapidly. Iodine acts in a very similar manner to nitric acid. The sulphuric acid which separates from the chloroform acquires a well-marked green fluorescence. If some of the chloroformic solution be poured into a capsule, the color rapidly changes to blue, green, and yellow, the changes apparently being due to traces of moisture. On addition of water the solution becomes paler, then blue, and finally nearly colorless, while showing a fine green fluorescence.

If cholesterol be heated cautiously with a drop of concentrated nitric acid, and the pale-yellow product treated with ammonium hydroxide before it has completely cooled, a fine yellowish-red tint is produced

If a mixture of 3 measures of concentrated hydrochloric acid and 1 of a solution of ferric chloride be evaporated with a little cholesterol, a reddish-violet coloration, changing to blue, is produced. Similar treatment with sulphuric acid and ferric chloride leaves a residue of a carmine color, which gradually passes to violet, and becomes scarlet on treatment with ammonium hydroxide

Burchard's modification of Liebermann's test is exceedingly delicate

but the reaction is shared by resin acids and other bodies. A small amount of the material is dissolved in 2 c.c. of chloroform, 20 drops of acetic anhydride are added, and a single drop of concentrated sulphuric acid. In the presence of cholesterol, a violet-pink coloration will appear.

Nagelvoort (*Analyst*, 1889, 217) obtained from a sample of cod-liver oil acicular crystals resembling phytosterol, but which gave the color-reactions of cholesterol (reddish-brown with sulphuric acid, turning to dirty green on the addition of water). On repeating the extraction, crystals of the usual form of cholesterol were obtained.

### Isocholesterol.

This body is isomeric with ordinary cholesterol and occurs with it in wool-fat. To separate the isomeric alcohols, the mixture should be heated for 30 hours in a sealed tube to 200° C, with four times its weight of benzoic acid or benzoic anhydride. The product is then repeatedly boiled with rectified spirit, when the excess of benzoic acid dissolves and the cholesteryl and isocholesteryl benzoates remain. By crystallising them from ether, the former is obtained in shining rectangular plates and the latter as a light crystalline powder which can be separated by decantation and elutriation. Cholesteryl benzoate melts at 150–151°, and the isomer at 190–191° C. By saponifying the ethers with alcoholic potash, and diluting the solution with water, the cholesterol and ischolesterol are precipitated.

So prepared, ischolesterol resembles the ordinary body, but melts at 137–138°, and solidifies on cooling to a brittle vitreous mass. A mixture of cholesterol with ischolesterol melts at a lower temperature than either body separately. Isocholesterol separates from its dilute solution in absolute alcohol in flocks, but a concentrated solution solidifies on cooling to a translucent jelly. From its ethereal solution it is deposited in needles.

When evaporated with nitric acid and afterwards treated with ammonium hydroxide, ischolesterol gives the same reaction as cholesterol (page 349), but it gives no color-reactions with sulphuric acid and chloroform, or with ferric chloride and a mineral acid.

With the Burchard-Liebermann test a (see page 349) yellow and afterwards a reddish-yellow coloration appears, with, at the same time, a green fluorescence.

Hot acetic acid dissolves ischolesterol readily, forming an unstable compound which loses its acetic acid on fusion. The true isocholesteryl acetate is obtained by digesting the alcohol with acetyl chloride



until the evolution of hydrochloric acid ceases, and then heating the mixture to 100° in a sealed tube. On removing the excess of acetyl chloride by evaporation, isocholesteryl acetate is obtained as an amorphous substance, melting below 100° and readily soluble in alcohol (compare "Cholesteryl Acetate," page 348).

Isocholesterol is *dextro-rotatory*, the specific rotation in ethereal solution for the sodium ray being 60°.

#### Phytosterol, $C_{27}H_{48}O$ .

Phytosterol, the "cholesterol of plants," has been found in the seeds of beans, peas, almonds, in maize and wheat, and in most vegetable oils, with the notable exception of olive oil and palm oil.

The reactions of phytosterol resemble those of cholesterol, but the two bodies differ in melting point and crystalline form. The crystals of phytosterol separated from a hot alcoholic solution appear in tufts of needles. These have the composition  $C_{27}H_{48}O + H_2O$  and a melting point which is usually stated at 132–134°. Bomer (*Zeit. f. Unter d. Nahr. u. Genuss*, 1898, 81), as the result of a number of examinations, finds a mean of 137.5°.

Solutions of phytosterol are levorotatory, the specific rotation for the sodium ray being 34.2°.

#### Isolation and Determination of Cholesterol and Phytosterol. Examination of Ether Residues.

For the separation of cholesterol and phytosterol from animal and vegetable matters containing it, the dried substance should be exhausted with ether, as described on page 20, the ether distilled off, and the residue saponified by alcoholic potash (page 44), the alcohol evaporated, and the cholesterol extracted from the aqueous solution of the resultant soap by agitation with ether, in the manner described on page 113. When oils or fatty matters are to be examined, they may be at once saponified by alcoholic potash.

When no other unsaponifiable matter is present, the ether-residue will consist solely of cholesterol and phytosterol, which therefore may at once be weighed, but more frequently a further purification is necessary. To ensure the complete absence of saponifiable matters it is desirable to repeat the treatment with alcoholic potash and re-extract the aqueous solution of the evaporated product with ether.

The estimation of cholesterol and phytosterol in fats is most conveniently determined by the method of Forster and Riechelmann (*Analyt.*, 1897, 131). 50 grm. of the fat are twice boiled, for about five

minutes at a time, with 75 c.c. of 95-96 per cent. alcohol, in a flask fitted with a reflux condenser, the flask being meanwhile well shaken. The separated alcoholic solution is mixed with 15 c.c. of 30 per cent. sodium hydroxide solution, and boiled on the water-bath, in a flask fitted with a condensation tube, until about one fourth of the alcohol has evaporated. The fluid is then evaporated nearly to dryness in a porcelain basin and the residue shaken up with ether. The ethereal solution is evaporated to dryness, the residue treated with a little ether, filtered, evaporated, and the residue crystallised from 95 per cent alcohol. Pure cholesterol can easily be distinguished from phytosterol by the forms and grouping of the crystals. If both bodies are present, the mixture crystallises in one form only, the crystals either approximating to the form of phytosterol, or if cholesterol is present in the greater quantity, differing from the pure crystals of either body.

Von Raumer (*J. S. C. I.*, 1898, 774) determines the amount of crude cholesterol and phytosterol in fats as follows. 50 gram. of the oil are saponified with alcoholic potash. The resulting soap is evaporated to dryness, reduced to powder, and extracted with 50 to 75 c.c. of ether in a Soxhlet apparatus, plugs of fat free cotton being placed above and below the layer of soap. The residue is saponified again with 10 c.c. of seminormal alkali, evaporated to dryness with sand, and re-extracted as before during two hours.

As an alternative method, the dried soap from 50 gram. of the oil may be subjected to cold extraction in a separating funnel, by exposure for one-half hour to 100 c.c. of ether, this operation being repeated twice with fresh quantities of 100 c.c. of the solvent.

By the first method the following results were obtained from 100 gram. of oil. Cottonseed oil, 0.7199 gram.; sesame oil, 1.3146 to 1.3256 gram.; lard, 0.2176 gram. By the second method, 1.351 gram. was obtained from sesame oil.

The results seemed to show that when the work is carefully done the second saponification and extraction are unnecessary.

The bodies most frequently occurring with cholesterol and phytosterol, in the "unsaponifiable matter" of which the ether residue is composed, are ischolesterol (page 350), wax-alcohols from sperm oil, wool-fat, &c., and various hydrocarbons. A partial separation of these bodies may be made by boiling the ether-residue with about three times its measure of alcohol, and filtering the liquid while hot. Hydrocarbons, e.g., petroleum products, vaseline, &c., remain chiefly undissolved. On cooling the alcoholic filtrate, with or without previous concentra-

tion, cholesterol and phytosterol will mostly deposit, while the alcohols from sperm and bottlenose oils remain in solution.

A more perfect separation of the constituents of a complex ether-residue, such as that yielded by "recovered grease" or the crude oleic acid obtained by distillation of such products, may be made by the following method (Schulze, *Jour f prakt Chem*, cxv 163) —The ether-residue is boiled for an hour or two with an equal weight of acetic anhydride, in a flask furnished with an inverted condenser. The hydrocarbons, such as petroleum, vaseline, cerasin, and paraffin, are not dissolved, but form an oily layer on the surface of the acetic anhydride, which latter should be separated while still hot from the hydrocarbons and boiled two or three times with water. This treatment removes the excess of acetic anhydride. The residue consists of acetates of the solid alcohols, and if boiled with sufficient alcohol will dissolve entirely, but on cooling the solution the cholesteryl acetate will crystallise out almost completely. The acetates of the alcohol radicles from sperm oil and the waxes (as also any ischolesteryl acetate) remain in solution, and are precipitated as an oily layer by pouring the liquid into hot water.

Lewkowitsch operates upon a known quantity of the alcohols, and thus determines the increase in weight at the same time (see table).

Further information respecting the nature and probable source of the acetates can be obtained by ascertaining their melting points and saponification-equivalents, as also the melting points and iodine absorption of the recovered alcohols resulting from saponification.

RADICLE	ALCOHOL			ACETATE	
	Melting Point, °C	Iodine Absorption	Percentage of Increase in Weight on Boiling with Acetic Anhydride (Lewkowitsch)	Melting Point, °C	Saponification-Equivalent
Dodecetyl, $C_{12}H_{25}$	24	0	Not determined	Liq. at ord temp.	224
Hexadecyl (Cetyl), $C_{16}H_{33}$	49.5	0	17.2	22-23	284
Octadecyl, $C_{18}H_{37}$	60	0	15.5	31	311.6
Cetyl, $C_{20}H_{41}$	79	0	10.6	65	179
Myristyl, $C_{22}H_{43}$	85-86	0	9.6	116.7	180
Cholesteryl, $C_{27}H_{49}$	147	68.3 <sup>1</sup>	11.3	92	471
Ischolesteryl, $C_{29}H_{51}$	137-138	68.3 <sup>1</sup>	11.3	Below 100	474
Phytosteryl, $C_{30}H_{53}$	132-136	68.3 <sup>1</sup>	11.3	.	474

<sup>1</sup> Calculated. Lewkowitsch (*J & C J*, 1892, 143) obtained for cholesterol iodine-absorption of 68.09 and 67.3.

The acetates of the wax-alcohol radicles saponify readily, that of cholesteryl acetate is more gradual, but is completed when the solution becomes clear. The alcohols will be separated on acidulating the soap solution, while acetic acid remains in solution, the behavior being the reverse of that with saponified fats.

Lewkowitsch (*J S C I*, 1892, 134) obtained the following results from an examination of the mixed alcohols from sperm oil and wool-fat:—

MIXED ALCOHOLS FROM	MELTING POINT, ° C	IODINE ABSORPTION	SAPONIFICATION EQUIVALENT OF THE ACETATE
Sperm oil . . . . .	25.5-27.5	64.6-65.9	295-348
Neutral Wool-fat . . . . .	"	36	348
Crude Wool-fat . . . . .	"	"	372

The separation of aliphatic alcohols from cholesterols has not as yet been satisfactorily accomplished. Lewkowitsch (*J S C I*, 1892, 135) has proposed a method based upon the conversion of the alcohols into fatty acids when heated with potash-lime, the cholesterols remaining practically unchanged by the treatment. In some experiments on alcohols from sperm oil, all except 4 to 6 per cent. were converted into fatty acids. On treating cholesterol in the same manner 93 per cent. was recovered unchanged.

Cochenhäusen (*J S C I*, 1897, 447) advises heating the mixture with sulphuric acid, by which the alcohols are converted into alkyl sulphates and the cholesterol into hydrocarbon "cholesterones." The former may be isolated by means of their sodium salts and the alcohol recovered by treatment with hydrochloric acid. See also Buisine's Method for waxes, page 224.

### Wool-Fat. Wool-Grease Suint.

*French*—Suint *German*—Wollfett; Wollschweissfett.

Sheep's wool contains a large amount of fatty matter of very peculiar character. It is excreted by all parts of the animal, but is found most abundantly about the breast and shoulders. The crude "yolk," as it is called, is largely soluble in water, and hence is removed by washing the wool, but the wool-fat or suint proper remains, and can

be extracted by carbon disulphide, petroleum spirit, ether, or other suitable solvent.

Thus obtained, wool fat is a yellow or brownish grease, having a peculiar disagreeable smell. It melts between  $39^{\circ}$  and  $43^{\circ}$  C., and has a specific gravity of about .973 at  $15^{\circ}$  C. It possesses the remarkable property of forming a very perfect emulsion with water, which when kept at the ordinary temperature exhibits no tendency to separate into its constituents.

Complete saponification of wool fat cannot be effected by boiling with alcoholic potash, except under pressure.

Chemically, wool-fat has a peculiar and complex composition, and the exact nature is still unknown. Cholesterol and isocholesterol are present and potassium salts of various fatty acids, some of them volatile. Contrary to the usually accepted statements, Lewkowitsch (*J. S. C. I.*, 1892, 136; 1896, 14) has found that wool-fat is not a mixture of cholesteryl and isocholesteryl stearates, palmitates, and olenates, as is shown by the low iodine absorption of both the fatty acids and the alcohols. The former were found to consist of hydroxy-acids, easily giving off the elements of water at temperatures little above  $100^{\circ}$  C., with formation of inner anhydrides or lactones. Oleic acid, if present, is in small amount. Besides cholesterol, a considerable proportion of lower saturated alcohols is present. No tritenyl esters have been found in wool-fat.

Darmstadter and Lifschitz (*J. S. C. I.*, 1897, 150) have reported the isolation of the following bodies:—*Lanocenic acid*,  $C_{30}H_{48}O_4$ , insoluble in water, but easily soluble in hot alcohol, from which it crystallises, on cooling, in plates of melting point  $103^{\circ}$ – $105^{\circ}$ ; *lanopalmitic acid*, melting at  $87^{\circ}$ – $88^{\circ}$  and solidifying at  $83^{\circ}$ – $85^{\circ}$  to a lustrous crystalline mass, and having the property of readily forming an emulsion with water; also *carnaubic* and *myristic acids*, an oily acid apparently *oleic*, and a volatile acid, possibly *caproic*. Among the alcohols, separated by absolute alcohol into several fractions, carnaubyl alcohol (saturated), and cholesterol were identified. The investigations of G. de Sanctis (*Chem. Zeit.*, 1895, 651) point to the presence also of *palmitic* and *cerotic* acids.

The results of Lewkowitsch's inquiries into the nature of wool-fat (*J. S. C. I.*, 1892, 135, 1896, 14) have led him to conclude that it is a true wax in the strict sense of this generic term. Natural wool-fat resembles beeswax, its closest relative, in that it contains a considerable proportion of free acid and a small amount of free alcohols, besides true waxes, and the term wool-wax should therefore be substituted for

wool-fat; but considering the fact that the commercial wool-fat is, as a rule, contaminated with fatty acids derived from the soap used in scouring the wool, it is more convenient to retain the term wool-fat for the commercial product. He proposes, therefore, that the name wool-wax be given to the neutral portion of the wool-fat. This consists of a mixture of true wax and alcohols, the former predominating considerably. The name wool-wax appears all the more desirable, as this neutral portion is now obtained in large quantities, both in the anhydrous and hydrated state, and confusion with the crude wool-fat is thereby avoided.

The following are the results of examinations made by Lewkowitsch, as well as some determinations made in the author's laboratory by W. Chattaway:—

WOOL-WAX (ESTERS AND FREE ALCOHOLS)

	LEWKOWITSCH	CHATTAWAY
Specific gravity at 98.5° (water at 15.5° = 1)		9017 <sup>2</sup>
Melting point . . . . .	31°-35° <sup>1</sup> 39°-41°	
Solubilizing point . . . . .	30°-30.2° <sup>1</sup>	
Percentage of KHO for saponification	10.24 <sup>1</sup>	9.83 <sup>2</sup>
Saponification-equivalent . . . .		901.7 <sup>2</sup>
Iodine absorption . . . . .	{ 25.8-28.9 <sup>1</sup> }	
	{ 17.1-17.6 <sup>2</sup> }	
Fatty acids, per cent . . . . .	59.8	
Alcohols . . . . .	43.6 51.84 <sup>2</sup>	

	MIXED FATTY ACIDS	MIXED ALCOHOLS
Solubilizing point . . . . .	40°	28° <sup>1</sup>
Melting . . . . .	41.8°	32.6°
Mean molecular weight . . . . .	327.5	239
Iodine absorption . . . . .	17.0	36 <sup>1</sup> 26.4 <sup>2</sup>

NEUTRAL ESTERS	
KHO for saponification, per cent . . . . .	9.69
Fatty acids, . . . . .	56.66
Alcohols, . . . . .	47.55

When extracted by means of solvents, wool-fat contains simply the constituents (fatty acids, neutral esters, alcohols, and potassium salts

<sup>1</sup> From raw wool-fat. <sup>2</sup> Prepared from "lanolin."

of lower fatty acids) natural to the wool. The following table represents the results of examination of wool-fat extracted by ether (Hering, *J S C I*, 1894, 1069).—

SOURCE	POTASSIUM SALTS IN ASH, CALCULATED TO POTASSIUM OxIDE	FREE AND KIIO RE- QUIRED	FIRST STAGE OF KIIO FOR SAPONIFICATION ON HEATING FOR ONE HOUR		UNSATURATED MAT- TER (AT 100° HOLZ)
			Open Flask	Closed Flask	
New Zealand Wool	4.9	14.3	10.60-10.82	11.05-11.07	43.06-43.91
Australian "	4.21	15.5	10.25-10.35	11.27-11.42	
South American "	9.27	11.2	8.82-9.11	9.80-9.89	33.15-44.65
Russian "	24.4	13.9	7.77-7.83	9.11-9.65	38.72-39.10

Wool-fat prepared by acidulating the suds obtained in the wool-scouring process is of variable composition. Potassium salts of the lower fatty acids are present in but small quantity, since these are removed in the first stage of the process, which consists in steeping the wool in luke-warm water. In addition to the compounds mentioned above as naturally present in the wool, it may contain unsaponified fat and mineral oil which had been added to lubricate the wool and fatty acids of variable character derived from the soap used in scouring. The product obtained in this way is called *recovered grease*, *wool-grease*, *brown grease*, and *Yorkshire grease*. In the United States it is incorrectly called "dégras" (For a description of true "dégras" see under that head.)

The analysis of wool-fat requires a departure from the usual methods. The potassium and other mineral constituents can be determined in the ash obtained on ignition. On saponifying the fat with alcoholic potash and extracting the soap in the manner described below, the *alcohols*, including cholesterol, are dissolved, and may be recovered by evaporation of the solvent, and examined as described on page 353. By treating the soap with acid, the *higher fatty acids* will be obtained, while the *lower fatty acids* can be determined by distillation in the usual way (p. 58). Foreign, saponifiable fats will be indicated by the presence of glycerol in the aqueous liquid separated from the fatty acids, and their amount will be roughly indicated by multiplying the glycerol found by ten.

*Free Fatty Acids*.—These are measured by treating a weighed portion of the fat with alcohol, and titrating with standard potassium hydroxide in the usual manner, the amount may be calculated from the mean molecular weight. Lewkowitsch (*J S C I*, 1892, 136)

separates the free fatty acids for the determination of the molecular weight as follows. The amount of alkali required for neutralisation is first ascertained by titrating a small weighed quantity of the fat. A larger weighed quantity is then dissolved in alcohol and nearly neutralised with the greater part of the alkali required, and the remainder is added cautiously until the solution becomes pink to phenolphthalein. The mixture of neutral fat and unsaponifiable matter, which rises to the surface, is dissolved in ether and separated from the soap solution, which is then repeatedly shaken out with ether. The ethereal extracts are united and washed repeatedly with water to remove all traces of soap. This stage of the process is very tedious on account of the emulsification of the two liquids. There is also formed an intermediate layer, consisting of soap of a higher fatty acid, which is not soluble in water, but dissolves readily in boiling alkaline solution of soap of the other acids. It is separated by filtration. The free fatty acids are thus obtained in two parts, those of the dissolved soaps and those of the difficultly soluble soaps. The ether dissolved in the soap solution is distilled off and the fatty acids set free by acidulating with hydrochloric acid. The solid soap on the filter is treated with boiling water and hydrochloric acid for the same purpose.

Cochenhausem (*J.S. C. I.*, 1894, 1100) modifies the above process as follows:—The neutralised wool-fat is shaken with 30 per cent. alcohol and the soap solution boiled down to dryness, dissolved in 50 per cent. alcohol, and exhausted with petroleum ether. In this process also insoluble soaps of higher fatty acids separate between the two layers as flocculent matter and must be filtered off.

As noted above, wool-fat contains hydroxylated fatty acids, which, on heating to a temperature of  $100^{\circ}\text{C}$  and over, lose the elements of water and form inner anhydrides or lactones. These are not completely hydrolysed by aqueous solution of potassium hydroxide, which, if used for the determination of the molecular weight on a sample which has been heated to dry it, would furnish results in excess of the truth. Error from this source is avoided by boiling the acids with standard alcoholic potassium hydroxide and titrating back the excess of alkali. In this way any anhydride which may be present is effectually hydrolysed.

*Saponification-equivalent*—As already noted, wool-fat is not completely saponified by simple boiling with alcoholic potassium hydroxide. Lewkowitsch (*J.S. C. I.*, 1892, 137), found that complete saponification could be effected by the use of double normal alkali under pressure. The fat and alkali should be contained in a copper flask



tightly closed, placed in boiling water and allowed to remain for from one to two hours, with occasional shaking. Identical results were obtained without pressure by the use of a freshly prepared solution of sodium ethylate. Herbig's experiments (*J. S. C. I.*, 1894, 1069) confirm these results so far as regards the saponification under pressure, but equally satisfactory results were not always secured by the use of sodium ethylate. Herbig found, further, that wool-fat contains esters that are easily saponified by alcoholic potassium hydroxide, and that, working under definite conditions, constant numbers for these are obtained. Heating over the naked flame was found to effect the result much more rapidly than by means of the water-bath, and the action is complete at the end of one hour's heating in a flask provided with a vertical condenser. By reason of its convenience, this method is often employed in the commercial valuation of wool fats. The table on page 357 shows some results obtained in this way compared with those obtained by saponification under pressure. In the latter determinations, double-normal alkali was used and the materials maintained at a temperature of 105°–106° C.

*Determination of Unsaponifiable Matter*.—The separation of the ethereal layer from the aqueous solution of saponified wool-fat and recovered grease is troublesome, an intermediate stratum of a very persistent nature being formed. C. Rawson has suggested the following plan.—

The sample is saponified with alcoholic potash in the usual way, and the resultant solution is evaporated in a porcelain basin placed over a small flame. Toward the end of the operation some powdered sodium acid carbonate is stirred in to neutralise the excess of alkali, and some sand also added. The residue is then dried at 100° and exhausted with ether in a Soxhlet tube. The ethereal solution is then evaporated to dryness, the residue boiled with water, and the solution agitated with ether, or the ethereal solution is at once agitated with water containing a little caustic soda to dissolve any soap it may contain, and then evaporated to dryness and the residue weighed.

A more satisfactory method is that of Herbig (*Analyst*, 1896, 47). From 1 to 25 grm. of the fat are boiled with seminormal potassium hydroxide for an hour, the excess of alkali neutralised with standard acid, and the whole washed into a beaker with boiling alcohol. The alcohol is evaporated, the solution heated to 70°–75° C, and the fatty acids precipitated with calcium chloride, the amount of which has been calculated from the saponification-equivalent. The precipitate is filtered off, well washed with dilute alcohol (1 to 20), and dried on the

filter *in vacuo*. When dry, it is extracted in a Soxhlet extractor with freshly distilled acetone for six hours, after which the acetone is evaporated, the extract washed with ether into a platinum basin, the ether evaporated, and the residue, which consists of the unsaponifiable matter and of the esters which cannot be saponified by the ordinary process of boiling with alcoholic potash, dried at 105° C and weighed.

The chief points to be observed are the purity of the acetone—the fraction boiling between 55.5° and 56.5° being used—and the temperature at which the calcium salts are precipitated. If too hot they fuse, and if too cold they become slummy, subsequent filtration being almost impossible in either case.

It is advisable to extract the cork of the extraction apparatus with ether, alcohol, and acetone.

For the estimation of the alcohols, free and formed by the saponification, it is necessary to saponify under pressure, precipitate with calcium chloride, and extract with acetone as described.

F. Ulzer and H. Seidel (*Analyst*, 1896, 260) propose to determine, instead of the saponification-equivalent, the total acidity number, as was recommended by Benedikt and Mangold in the case of wax. This number is the amount of potassium hydroxide (expressed as milligrams per gram) required to neutralise the mixture of fatty acids and fatty alcohols obtained by saponification and decomposition of the soap with acid. 20 gm. of potassium hydroxide are dissolved in 20 c.c. of water in a porcelain basin holding from 350 to 500 c.c., and the solution heated to boiling for about a minute, the heating continued on a water-bath until a thick, uniform soap is obtained, and the basin finally placed for two hours in the water-oven to complete the saponification. The soap is dissolved in about 250 c.c. of boiling water and decomposed with 40 c.c. of hydrochloric acid previously diluted with water. The clear fatty layer is repeatedly washed with boiling water until the washings are free from acid, and then dried in the water-oven. From 5 to 6 gm. of the dry mixture of fatty acids and alcohols are weighed accurately and titrated with *alcoholic* potassium hydroxide with the precautions noted above in the determination of the molecular weight. The authors conclude that for the technical examination of a wool-fat sufficient data are furnished by the determination of the acid value (*i.e.*, the milligrams of potassium hydroxide required to neutralise the free fatty acids of one gram), the total acidity number, the iodine number, and the Reichert-Meissl number, together with a gravimetric determination of the unsaponifiable matter.

Lewkowitsch (*J S C I*, 1892, 141, and *Chem Anal of Oils, Fats, and Waxes*) gives the following data from the analysis of a wool fat — The volatile acids were determined by the Reicheit process and their mean molecular weight assumed to be 104 ( $C_8H_{16}O_2$ ). The total free and combined fatty acids were well washed to free them from soluble fatty acids, and their molecular weight found to be 332

Volatile acids from 1 gram required,	0.121 c c normal KOH.
Free insol acids " " "	0.586 " " "
Total " " " " "	2.19 " " "
Combined insol acids (by difference).	1.48 " " "
Unsapifiable matter, . . . . .	36.47 per cent

And therefore,

Volatile fatty acids = $0.124 \times 10.2 =$	1.26	" "
Insoluble free fatty acids = $0.586 \times 33.2 =$	19.45	" "
Combined insol fatty acids (hydrated) =		
$1.48 \times 33.2 =$	49.13	" "
Total unsapifiable matter, .	36.47	" "
	<hr/> 106.31	" "

The excess over 100 per cent is of course due, in part at least, to hydration incident to the saponification

**LANOLIN** —On account of its property of readily forming with water an emulsion easily absorbed by the skin, wool fat, purified by various patented processes, has come into extensive use as a basis for ointments and salves. Two preparations are recognised by the British Pharmacopœia—*Adeps Lanæ* and *Adeps Lanæ Hydrosus*. The current U. S. Pharmacopœia recognises only the latter form. It is commonly known as "Lanolin," and consists of about 75–80 per cent of wool-wax with 20–25 per cent of water. It is usually white or slightly yellow, and of salve-like consistence. It does not turn rancid. According to Liebrich, it should be free from all traces of chlorine, metals, glycerol or its esters, soaps, saline matters, and mechanically intermixed impurities or coloring matters, and it should not have any disagreeable odor. On rubbing on blue litmus-paper no reddening should occur.

The U. S. Pharmacopœia prescribes the following requirements for lanolin. —

When ignited it should leave not more than 0.1 per cent of ash, which should not have an alkaline reaction to litmus (absence of *alkalies*).

If 2 gram are dissolved in 10 c c of ether and mixed with 2 drops of phenolphthalein solution, a colorless liquid should result (absence of *free alkalies*), which should be decidedly reddened by 1 drop of normal potassium hydroxide (absence of *free fatty acids*).

If 10 grm be heated together with 50 c.c. of water on a water-bath, until the fat is melted, there should result an upper translucent and light-yellow fatty layer, and a lower, clear aqueous layer, which latter should not yield glycerol on evaporation, and when a portion of it is heated with potassium hydroxide solution it should not emit vapors of ammonia.

Distilled wool-grease is a product obtained by distilling wool-fat with the aid of steam. The lighter portions, "olein," separated by cooling, are used for lubricating wool, and the more solid fractions "stearine," in the manufacture of soap and candles. It has also been used to adulterate tallow. According to Lewkowitsch (*J S C I.*, 1892, 142), but a small proportion of the esters originally present in the wool fat are found in the distilled product, the greater portion being decomposed into fatty acids and hydrocarbons. The fatty acids, especially the higher members of the series, are further associated into hydrocarbons and acids of lower molecular weight. Hydrocarbons are also formed by the decomposition of the free alcohols, a part of which, however, distil unchanged. The nature of these hydrocarbons is not well understood, and no means is known of distinguishing them from hydrocarbons intentionally added.

The examination of distilled wool-grease is conducted upon the same general lines indicated in the case of wool-fat. Lewkowitsch obtained the following results from a sample obtained by the distillation of recovered grease, the analysis of which is stated on page 361 —

Free fatty acids, . . .	54.91 per cent
Combined fatty acids,	7.02 " "
Unsaponifiable,	38.80 " "

For other analyses of distilled wool-grease see page 265.

Alcoholic potassium hydroxide should be used in the determination of the molecular weight.

The fatty acids may also be determined with sufficient accuracy by the usual gravimetric method.

### Sod Oil. Dégras.

*French*—Dégras, Moellon. *German*—Lederfett, Weissbrühe, Gerberfett.

Dégras is the waste fat obtained in the chamoising process and largely used in dressing leather. The chamoising process consists essentially in oiling the suitably-prepared skins with whale- or cod oil (i.e., the lower grades of cod-liver oil), stamping them in the stocks, and placing them in heaps, so that a fermentative change attended with develop-

ment of heat is brought about. The process is complete when the skins have acquired the usual yellow color of chamois leather. Under these conditions, oxidation of the oil takes place, and a portion of it combines with the skin, from which it cannot be removed by the usual solvents. About an equal quantity of uncombined oil is also mechanically enclosed in the skin. After being well scraped with a blunt knife, by which much of the excess of oil is removed, the skins are washed with lye and the emulsion treated with acid; the fatty matter which rises to the surface is added to the oil already obtained by scraping. The product so obtained constitutes the so called "sod oil." This is the method largely used in Germany and England. The following process employed in France is also used in England to a considerable extent.—The treatment by oiling, stocking, and fermenting is carried out for a shorter period, so that a larger proportion of uncombined oil remains in the skins. This is removed by wringing or by draulic pressing, and constitutes the "moellon" or "dégrias" of commerce. The remaining uncombined oil is removed by washing with lye and treatment with acid, and is usually added to the product. The moellon of commerce is said to be invariably mixed with untreated oils. Moellon contains less fibre, mineral matter, and water than sod oil.

Jean found that dégras (moellon) contains from 10 to 20 per cent of water, and that the property of forming an emulsion with water depends upon the presence of an oxidation product of the oil formed during the chamoising process. He describes it as a "resinous substance," insoluble in petroleum spirit, but soluble in alcohol and ether. It is saponifiable, but, unlike ordinary fat, the soap formed is not precipitated from alkaline solution by the addition of salt. The melting point was stated to be 65°–67°. Simand has given it the name *dégas-former*. According to him it is insoluble in petroleum spirit, benzene, and almost insoluble in ether. It is soluble in alkaline solutions, from which it is precipitated by the addition of acid. It was also found in all animal and marine oils. Fahrion (*J S C I*, 1891, 557) regards it as a mixture of hydroxy-fatty acids and anhydrides. It is an oxidation product, and experience has shown that those marine animal oils which absorb oxygen readily are the most suitable for the preparation of dégras. Fahrion found an iodine-absorption of 65.9 per cent in dégras former. Rubsam found 98.8 per cent in sample No. 1 on page 368. According to Fahrion (*J S C I*, 1891, 558), dégras former contains no nitrogen, that found by Etner being due to impurities.

Dé gras-former is said not to exist in the free state in dé gras, but forms a part of the saponifiable matter which is readily soluble in petroleum spirit, in which the dé gras-former itself is insoluble.

C. Baron (*J. S. C. I.*, 1897, 922) prepares an artificial dé gras as follows.—1000 kilos of neutral wool-fat (extracted by petroleum spirit) are placed in a tinned steel vessel with 5000 kilos of cod- or whale-oil. The liquid is heated by a steam coil, agitated for three hours, then allowed to rest and cool for the same period, and the water withdrawn. The water is again heated to 40°, 150 kilos of hydrogen peroxide and and 450 kilos of water added, and the whole agitated for five hours at a pressure of 2 atmospheres. The resulting product is said to form an excellent mœllon, having a yellow color and being easily emulsified and absorbed by the skins. It is important that the wool-grease be free from sulphuric acid, lest this should dissolve traces of iron, and so cause darkening of the leather.

#### EXAMINATION OF DEGRAS

Water is determined, according to Simand, by weighing 25 grm. of the sample in a tared porcelain basin provided with a short thermometer as stirrer, adding 50–100 grm. of blubber or other oil previously dried by heating to 105° C., heating the mixture to the same temperature, and determining the loss in weight. Ruhsam makes the determination by heating 2–3 grm. of the sample in a weighed platinum crucible until an empyreumatic odor indicates the complete dehydration of the fat.

French dé gras usually contains from 10 to 20 per cent. of water; sod oil may contain as much as 40 per cent.

*Free Acid*—*Mineral acids* may be detected as described on page 104. The amount is determined by boiling a weighed quantity of the sample with water and separating the watery solution, which will contain the mineral acids as well as any soluble fatty acids, the determination of the former is made by adding methyl-orange and titrating with standard alkali until the point of neutrality is reached. The *soluble fatty acids* are then determined by adding phenolphthalein and titrating a second time.

*Free fatty acids* may be determined in the residue insoluble in water by dissolving in alcohol and titrating as usual. They are usually calculated to oleic acid.

*Ash*—This is determined in the usual manner. It should be tested for iron. According to Simand, even as low a proportion as 0.05 per cent. of ferric oxide has a distinctly injurious effect.

The ash of moclion is usually less than 0.1 per cent., that of sod oil may amount to several per cent.

*Fragments of hide* may be determined in the residue left from the solution in petroleum spirit, which is dried, weighed, and incinerated. The loss on incineration may be taken to represent, roughly, the hide fragments.

*Unsapoifiable matter* may be determined in the usual manner as described on page 113.

*Dégras-former*—Simand makes the determination as follows—20 to 25 gm. of the sample, according to the amount of water present, are saponified in an Erlenmeyer flask, with a funnel placed in the mouth, using a solution of about 5 to 6 gm. of solid sodium hydroxide in 10 c.c. of water and 50 to 60 c.c. of alcohol. The alcohol is evaporated, the soap dissolved in water, and the fatty acids liberated by hydrochloric acid. The liquid is then warmed until the fatty acids have formed a clear oily layer and the dégras-former has collected in lumps. It is then allowed to cool and the acid water separated from the undissolved portion. This latter is washed several times with boiling water, the washings added to the acid liquid, and the mass remaining in the flask (consisting of the dégras-former, fatty acids, and unsapoifiable matter) is dried at 105° C. The acid liquid and washings are neutralised with ammonium hydroxide, evaporated to dryness, redissolved in a small amount of water, the solution feebly acidified with hydrochloric acid and the small amount of dégras-former thus obtained (which had been dissolved in the aqueous liquid) separated by filtration, washed, dried, and added to the contents of the flask. It is then extracted with 100 to 120 c.c. of petroleum spirit, which dissolves the fatty acids and leaves the dégras-former and some albuminous materials. The residue is dissolved in alcohol by warming, the solution filtered, the filtrate evaporated to dryness, and the residue weighed as dégras-former. The process is said to be accurate within 0.5 per cent. The petroleum spirit may be evaporated and the residual fatty acids weighed and examined.

Dégras, according to Simand, is pure and genuine only when it contains at least 12 per cent. of dégras-former. It may contain as much as 17 per cent.

Jean determines the proportion of "resinous substance" as follows: A weighed quantity of dégras is saponified and the watery solution or the soap extracted with ether to remove the unsapoifiable matters. The soap solution is boiled to drive off the ether, and precipitated while hot with excess of pure sodium chloride. After cooling, the colored

liquid is filtered from the separated soap, the filtrate collected in a flask, and acidified with hydrochloric acid. The "resinous substance" separates in flocks, which on boiling unite and adhere to the side of the flask. The liquid is cooled, shaken out with ether, the ethereal solution evaporated, and the residue dried and weighed.

Jean considers that a specific gravity of the oil extracted from dégras of less than 920 indicates the presence of foreign fats, *eg*, wool fat, oleic acid, and tallow. The specific gravity of the oil from dégras made from fish- and whale-oil is given as 949 to 955. The presence of tallow is also indicated by the higher melting point of the fatty acids. In the examination of artificial dégras, Simand takes into consideration, in addition to the ash and water, the following points:—

- 1 The dégras-former, which may be derived from a small quantity of admixed true dégras or from the oils
- 2 The wool-fat.
- 3 Hydrocarbons (vaseline)
- 4 Colophony.

To determine the dégras former, Simand proceeds as with genuine dégras, but substitutes ether for the petroleum spirit, since the wool-fat acids are dissolved by the former in the cold.

The determination of the amount of wool-fat is as yet an unsolved problem. The detection of cholesterol would not, in itself, suffice, as it is a natural constituent of the fish oils used in the manufacture of dégras. Lewkowitsch points out that by the ordinary methods of saponification, a portion of the wool-fat would probably be found in the unsaponifiable portion, and that by again saponifying under pressure a definite saponification value would point to the presence of wool-wax.

Benedikt (*Anal d Fette u Wachsten*) states that by determining the amount of cholesteryl acetate (see page 353) a very rough approximation of the amount of wool-fat may be obtained. Wool-fat furnishes percentages of cholesteryl acetate varying from 9.59 to 18.71 per cent.



Resin may be determined as on page 107, and hydrocarbons as on page 110

Jean gives the following example of examinations of dégras:—

	1	2	3	4	5	6	7
Water per cent	18 00	14 84	12 94	28 90	19 20	5 30	8 90
Ash "	0 25	0 13	0 55	0 70	0 07	0 25	1 21
Hide fragments "	0 30	0 30	0 09	0 58	0 27		1 50
Oils "	60 71	74 05	80 00	86 03	75 06	84 87	72 15
Unsaponifiable matter "	6 84	6 05					
"Resinous substance" "	4 00	4 05	5 81	3 52	4 80	9 46	10 15

Simand gives the following results —

		DÉGRAS-FORMER PER CENT	MELTING-POINT OF FATTY ACIDS, ° C	SOAP, PER CENT	ORIGINAL DÉGRAS	
					Hide-Fragments, Per Cent	Water, Per Cent
French dégras (Anhydrous)	{ 1	10 14	18 0-28 5	0 73	0 07	16 5
	{ 2	18 43	28 5-29	0 49	0 12	20 5
	{ 3	18 10	31 0-31 5	0 68	0 18	13 0
Sed oil (Anhydrous)	{ 1	20 57	33 5-34	3 95	5 7	35 0
	{ 2	18 63	27 5-27	3 45	5 9	28 0
	{ 3	17 84	28 0-28 5	3 00	4 5	30 5

The table on the following page gives the results of an extended series of examinations of dégras by R. Ruhsam (*J. S. C. I.*, 1891, 639). Samples 1 to 9 are French artificial dégras, No 10 is a so called "emulsion 'fat", No 11 is a genuine dégras from the cod oil No 12

The iodine-absorptions were determined as usual, the insoluble fatty acids being first freed from dégras-former by solution in petroleum spirit. It will be noted that the figure for genuine dégras is much higher than that of the artificial samples. The acetyl values were determined by the method of Benedikt and Ulzer, and are of value only for comparison with each other. (See page 245)

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
No of SAMPLE	WATER PER CENT	Iodine Absorption, PER CENT			ACID No	SAPONIFICATION No	ETHER No (DIFFERENCE BETWEEN 6 AND 7)	CONSTANT ACID No	CONSTANT SAPONIFICATION No	CONSTANT ETHER No (DIFFERENCE BETWEEN 9 AND 10)	ACID No	SAPONIFICATION No	ACID No (DIFFERENCE BETWEEN 12 AND 13)	ETHER No (DIFFERENCE BETWEEN 14 AND 15)
		Degras	Insoluble	Fatty Acids										
1	19.1	74.7	70.5	73.1	37.7	110.4	97.7	185.5	224.3	38.8	181.0	280.0	99.0	60.2
2	12.9	64.2	58.6	52.7	72.7	110.4	70.5	102.8	131.5	23.7	126.6	164.7	72.1	43.4
3	32.4	77.4	75.4	90.4	46.2	110.7	70.5	102.8	131.5	23.7	126.6	164.7	72.1	43.4
4	35.9	78.4	76.4	90.4	50.1	134.8	84.7	142.0	155.7	45.4	129.9	196.1	67.2	23.8
5	16.4	77.8	75.3	76.2	52.7	137.4	84.7	163.5	185.9	23.2	137.0	237.0	80.0	49.2
6	11.6	76.6	76.5	75.7	64.9	108.8	43.9	175.8	249.6	53.8	171.0	237.0	66.1	43.7
7	13.9	86.7	85.9	88.9				182.5	215.6	53.1	178.7	242.4	11.5	67.7
8	16.2	85.6	83.4	102.7	28.9	100.8	71.9	186.7	197.1	100.4	92.8	175.4	62.6	0.6
9	16.2	85.6	83.4	102.7	28.9	100.8	71.9	186.7	197.1	100.4	92.8	175.4	62.6	0.6
10	74.4	79.3	73.0	73.0	54.1	141.2	80.2	179.5	210.2	30.7	180.1	217.0	36.9	6.2
11	127.7	442.3	427.4	427.4	54.1	141.2	71.1	179.5	210.2	30.7	180.1	217.0	36.9	6.2
12	125.7	106.0	106.0	101.9	186.0	186.0		180.6	213.2	33.9	182.2	215.7	65.5	3.7
Mean of 1-10		78.5	77.6	77.7	60.4	121.2	70.8	160.2 (except No 8)	195.5 (except No 8)	35.2 (except No 8)	140.2	221.3	72.1	

### Cloth Oils.

Cloth oil or wool oil is a trade term for all materials used in lubricating wool before spinning, or rags before grinding and pulling. Since the success of the subsequent dyeing operations is in a great measure dependent upon the thoroughness with which these oils are removed by scouring, mineral oil or, in general, any unsaponifiable matter is objectionable.

Mineral oils are emulsified by soap solutions and removed in great part, but not completely, by ordinary scouring. With the better grades of goods even a small proportion of these oils is harmful, but with low grades it is permissible to use a strongly alkaline soap, by which the mineral oil is to a great extent removed.

According to Horwitz (*J S C. I.*, 1890, 937) cholesterol may be present in the cheapest grades of olive oil in sufficient quantity to cause spotting of the dyed fabric. A sample of oil used to lubricate a wool which exhibited this condition was found to contain 3 per cent of cholesterol, and other samples were found to contain as high as 4 per cent.

Olive, lard, and neatsfoot oils, and commercial oleic acid ("red oil," "elaine," "oleine") are largely employed, and when of good quality are the most suitable. Besides these, however, wool-grease, distilled grease, and seek oil (the recovered grease from the scouring of various silk, woolen, and cotton goods) are employed. The cheaper oils in the market consist of one or more of the above, mixed with more or less mineral oil. So-called "emulsion oils," consisting of oil or "oleine" held in suspension in a solution of soap, or of borax and Irish moss, and also simple solutions of soap are employed. The latter are prepared from castor oil or nicotinsulphuric acid.

An important factor to be considered in judging of the suitability of an oil for this purpose is its liability to cause spontaneous combustion. All oils that absorb oxygen are dangerous in this respect. Mineral oils, while not open to this objection, are still considered dangerous by reason of the facility with which a fire, once started, will spread in their presence. An examination directed to these points is all the more important in view of the higher rate of insurance which may be charged in some countries when oils considered unsafe in this respect are employed. In Great Britain the rating is based upon the nature of the oil, the proportion of unsaponifiable matter, and the flash test. The lowest rate is charged when an olive oil, lard oil, or "oleine" is used containing not more than 10 per cent of unsaponifi-

able matter, or a fish or manufactured oil containing not more than 30 per cent of unsaponifiable matter and having a flash point not under  $167^{\circ}\text{C}$ . The highest rate is charged in the presence of drying oils or of more than 50 per cent. of unsaponifiable matter.

The "flash point" of an oil intended for this purpose may be determined very simply by placing 50 cc in a porcelain dish or crucible, in a sand-bath, heating with constant churning, and noting the temperature at which a flash across the surface is produced when a small flame is brought near.

A satisfactory test of the liability of an oil to inflame spontaneously may be made by means of Mackey's "Cloth-oil Tester" (*J S C I*, 1896, 90) The apparatus consists of a cylindrical metal oven surrounded by a water jacket. The dimensions are as follows:—Outside, 8 in high and 6 in. diameter; inside, 7 in high and 4 in. diameter. The tubes A and B are  $\frac{1}{2}$  in internal diameter and 6 in. long measured from the lid. The depth inside with the lid on is  $6\frac{1}{2}$  in. A lid packed with asbestos wool fits on the top, and the tubes A and B serve to maintain a current of air through the oven. Care should be taken that the steam from the water jacket is neither drawn down B nor warms A. C is a cylinder made of a piece of wire gauze (24 meshes to the inch) 5 by 6 in., forming a roll 6 in. long and  $1\frac{1}{2}$  in. diameter. In this cylinder is placed 7 gm. of ordinary bleached cotton-wadding, previously impregnated with 14 gm of the oil under

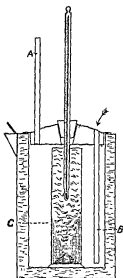


FIG 13.

examination, and occupying the upper  $4\frac{1}{2}$  in of the cylinder

The water being brought to the boiling-point, a thermometer is inserted in the oiled cotton contained in the gauze cylinder, which is then placed in the bath, the thermometer being allowed to protrude through a cork in the opening shown in the lid. The water is kept boiling and the temperature read at the end of an hour. An oil attaining a temperature of  $100^{\circ}\text{C}$  or over at the end of this time is to be regarded as dangerous. The following are the results of experiments on various oils.—

OIL USED	TEMPERATURE AT THE END OF			MAXIMUM
	One Hour	One Hour, Fifteen Minutes	One Hour, Thirty Minutes	
Cottonseed	125	242	.	H M
"	121	242	282	242 in 1 15
"	128	212	225	284 " 1 35
"	124	210	.	225 " 1 30
"	116	192	200	249 " 1 35
"	118	191	202	209 " 1 30
"	117	190	194	202 " 1 30
"	112	177	204	194 " 1 30
Olive, fatty acids	114	177	.	211 " 1 45
" " " "	105	165	.	196 " 1 25
" " " "	102	135	208	203 " 1 55
White Australian olive	103	115	191	226 " 1 45
Olive, with 1 per cent free fatty acid	98	102	104	240 " 1 45
" Oleine	98	101	102	241 " 3 25
" Ninety-seven per cent oleine	98	100	102	110 " 2 8
Belgian "oleine"	98	99	100	172 " 3 15
Olive, neutral	98	100	101	173 " 5 10
" "	97	100	101	245 " 5 15
" "	97	100	101	228 " 4 30
" "	97	100	101	235 " 4 55

The chemical examination of cloth oils is made by the application of the principles and methods already laid down. An estimation of the amount of the unsaponifiable matter is important, and if *hydrocarbons* are present the flash point should also be determined. The iodine number will aid in the detection of *drying oils*. The examination of commercial oleic acid is given in detail on page 262, it is to be especially tested for unsaponifiable matter and for linseed oil acids. *Resin* should be looked for in the fatty acids separated from the saponifiable portion as described on page 107. See also under "wool-fat" and "distilled wool-grease". Free mineral acid, which is especially apt to be present in commercial oleic acid, is objectionable on account of its corrosive action on card-teeth.

In the case of "emulsion oils" the fatty matter may be separated by treatment with acid and examined as above. *Gelatins* or *gummy matters* used in preparing the emulsion may be separated by addition of alcohol.

## ADDENDA.

To page 66

Hebner (*Analyst*, 1895, 49) has proposed to determine the bromine-absorption of oils gravimetrically, the method possessing, among others, the advantage that the products of the reaction are obtained in a form that their physical properties may be afterwards investigated. A small, wide mouthed flask is carefully weighed, and from one to three grm. of the fat placed in it, dissolved in a few c.c. of chloroform, and pure bromine added, drop by drop, until decidedly in excess. Both the chloroform and bromine must be previously tested in a blank experiment to make sure that they yield no appreciable residue. The flask is heated on the water-bath until most of the water is driven off, a little more chloroform is added, and the mixture is again heated, the chloroform vapor helping to drive off the excess of bromine. The addition of chloroform may be repeated. The flask and contents are placed in an air-bath and kept at 125° C. until the weight is constant; this takes several hours. A little acrolein and hydrobromic acid escape during the drying; the residue in some cases darkens slightly, in others, a clear yellow product is obtained. Drying at 100° C. does not furnish satisfactory results.

The following are some results, compared with Hubl's figures upon the same samples. For comparison, the gain in weight is calculated to iodine by multiplying by 1.587.—

SUBSTANCE USED	IODINE BY HUBL	IODINE CORRESPONDING TO BROMINE, GRAVIMETRICALLY
Olive oil	80.3	81.5
"	80.2	79.9
"	80.6	80.7
Lard	65.7	64.4
"	"	61.6
"	63.2	64.1
"	60.1	61.4
Maize oil	122.0	123.2
Butter-fat	34.0	34.3
Mutton fatty acids	48.1	47.8
Castor oil	83.0	69.6
Boiled linseed oil	132.5	159.5
Almond-oil fatty acids		102.3

For almond oil the Hubl figure was not determined, but calculating upon 95.5 per cent of fatty acids the figure 102.3 for the fatty acids corresponds to 97.7, given by Hubl for pure almond oil.

Hegner makes the following comments upon these figures.—“It will be seen that in most cases the iodine figure calculated from the gravimetric bromine-absorption is in satisfactory approximation to the Hubl number, considering that that number is liable to variations of from 1 to 2 per cent, even in duplicate analyses (Author and Zuk, *Zett. f. Anal. Chem.*, 1892, p. 536); but in the case of castor oil the bromine process as used by myself gives a substantially lower result than the Hubl method, while in that of the sample of boiled linseed oil the reverse is the case. Whatever the explanation may be, and without desiring to generalise upon such scanty data, it is remarkable that in both those cases in which the oils contained more oxygen than do ordinary oils the figures are substantially different. This difference may be worthy of further investigation. Fahlén (*Chem. Zeit.*, 1892, 1472) has already shown that the behavior of castor oil towards Hubl's solution is anomalous.”

R. Williams has published the following results of examinations of linseed oil by this process (*Analyst*, 1895, 276) —

KIND OF OIL	HUBL NUMBER	BROMINE DETERMINED GRAVIMETRICALLY	IODINE CORRESPONDING TO BROMINE
Raw linseed oil . .	183.2	114.2	141.2
" " " "	182.9	120.7	191.5
" " " " "	185.2	110.1	182.7
" " " " " "	195.5	119.2	184.2
" " " " " "	194.9	119.6	189.8
" " " " " "	195.1	118.4	189.5
Boiled linseed oil, thin	175.1	111.3	176.6
" " " " "	163.0	112.1	178.4
" " " stout	99.5	65.6	104.1
" " " very stout	96.9	59.5	95.1

Lewkowitsch, (*J. S. C. I.*, 1896, 859) and Jenkins (*J. S. C. I.*, 1897, 193) have noted that in some cases the brominated product appears to lose weight indefinitely on drying.

Wys (*Analyst*, 1898, 240) has proposed a new method for determining the iodine absorption of oils based upon the use of hypiodous acid, which is stated to be the substance chiefly concerned in the Hubl process. The fact that the substance decomposes readily ( $5\text{HIO} = \text{HIO}_3 + 2\text{H}_2\text{O} + 4\text{I}$ ) prevents its employment successfully at first hand. It was found best to obtain the acid by the action of water on

iodine chloride ( $\text{ICl} + \text{H}_2\text{O} = \text{HCl} + \text{HIO}$ ), choosing a solvent which contained so much of the former as would decompose nearly the whole of the latter, and at the same time not be oxidised by the hypoiodous acid. Good results were obtained with a solution of iodine chloride in 95 per cent acetic acid. This was prepared by dissolving 13 grm of iodine in a liter of acetic acid, determining the "halogen content" of the solution and passing in a current of chlorine (free from hydrochloric acid) until the "halogen content" was doubled. With a little practice this point is said to be readily discernible by the change in color. The solution is employed as Hubl's solution, except that the time required for absorption is greatly reduced. With oils of low iodine values, the absorption is said to be complete in four minutes, and with those of higher value not more than ten minutes will be necessary if too much oil be not taken.

The following are results compared with those of the Hubl process

	EXCESS OF IODINE, PER CENT	TIME OF ABSORP- TION	IODINE VALUE
Linseed oil	68	4 hours	180.91 (Hubl)
"	57	5 minutes	181.58
"	57	7 "	182.25
"	57	10 "	182.17
Liver oil	61	4 hours	180.04 (Hubl)
"	47	5 minutes	164.79
"	52	7 "	165.74
"	65	8 "	166.51
"	62	9 "	166.23
Maize oil	68	4 hours	124.87 (Hubl)
"	65	3 minutes	127.55
"	64	6 "	128.56
"	64	7 "	128.38
Poppy oil	69	4 hours	119.36 (Hubl)
"	69	3 minutes	119.66
"	57	7 "	119.67
Sunflower oil	70	4 hours	117.81 (Hubl)
"	69	3 minutes	118.02
"	63	7 "	119.01
Sesame oil	69	4 hours	110.35 (Hubl)
"	68	5 minutes	111.87
"	57	7 "	111.75
Cottonseed oil	68	4 hours	108.76 (Hubl)
"	59	3 minutes	110.07
"	59	7 "	109.63
Rapeseed oil	68	4 hours	102.06 (Hubl)
"	65	3 minutes	103.08
"	61	7 "	103.33
Earthnut oil	74	4 hours	87.26 (Hubl)
"	70	2 minutes	86.89
"	70	3 "	87.13
"	70	7 "	87.25
Olive oil	70	4 hours	83.27 (Hubl)
"	70	3 minutes	84.39
"	70	7 "	84.45



In almost every case the values given by the new solution were higher than the ordinary Hubl values, but they are claimed to be more correct by reason of the results obtained with purified allyl alcohol. This has a theoretical iodine value of 435. By Hubl's process Lewkowitsch obtained values varying from 349 to 376. Using an excess of 75 per cent of iodine, Wijs obtained an iodine value of 425 by Hubl's process, whilst with iodine chloride in acetic acid (the excess of iodine being the same) his results were after 5 minutes 434.1 and after 10 minutes 436.8

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**A Method of Analysing Oxidised Oils.** W. Fabrian (*Zeit angew Chem.*, 1898, 781-785).—From 2 to 3 grm. of the oxidised oil are saponified with 10 c.c. of 8 per cent. alcoholic potash on a boiling water-bath. The alcohol is evaporated, the soap dissolved in hot water, and the solution decomposed with hydrochloric acid in a separatory funnel, shaken with 25 c.c. of petroleum spirit, and allowed to stand over night, when the liquid will separate into two clear layers, with a stratum of solid oxy-fatty acids at the line of junction. As the non-volatile acids are all contained in the petroleum layer, it is unnecessary to again shake out the aqueous layer with petroleum spirit. After running off the lower liquid the petroleum layer is withdrawn from above, leaving the oxy-fatty acids in the funnel. If the quantity is considerable, it may enclose unoxidised fatty acids; and it is therefore advisable to dissolve the mass in a dilute solution of soda or ammonia, and repeat the treatment with petroleum spirit after acidifying with hydrochloric acid.

The united petroleum spirit extracts are evaporated, and the residue, consisting of the unoxidised fatty acids and unsaponifiable matter, dried to constant weight (1). It is then dissolved in 25 c.c. of 90 per cent. alcohol and titrated with semnormal alkali, the milligrams of KOH being calculated on the original oil. The number thus obtained, which the author terms the "inner saponification value," furnished a measure of the non-volatile and unoxidised fatty acids.

The neutral alcoholic solution is extracted with petroleum spirit, the extracts washed with alcohol, the petroleum spirit evaporated, and the residue of unsaponifiable matter dried and weighed (2).

The difference between (1) and (2) gives the quantity of non-volatile fatty acids, molecular weight of which can be calculated from the inner saponification value.

The oxy-fatty acids left in the separatory funnel are dissolved in hot alcohol, the solvent evaporated, the residue dried to constant weight, ignited, the ash deducted, and the difference taken as the oxy-fatty acids (3).

The sum of 1 + 3 gives the *Hehner* value.

The following results were thus obtained with cottonseed oil and three oxidation products, which were prepared by exposing the oil on wash-leather for eight and twelve days, respectively. The leather was cut into fragments and extracted with cold petroleum spirit, furnishing products A and B. The second leather still contained a considerable amount of product insoluble in petroleum spirit, which was subsequently extracted from it with cold ether (B<sub>1</sub>). It was a thick yellow oil, soluble in alcohol.

	COTTON-SEED	A	B.	B <sub>1</sub>
Iodine value . . . . .	108.8	55.4	46.3	29.1
Acid value . . . . .	2.2	13.3	13.8	33.4
Saponification value . . . . .	190.4	223.1	227.5	271.3
Inner saponification value . . . . .	186.9	128.8	128.0	74.4
Hehner value . . . . .	94.22	85.34	83.82	74.20
Unsaponifiable matter, per cent. . . . .	1.10	1.11	1.28	0.72
Oxy-fatty acids, per cent. . . . .	0.27	20.70	10.43	37.72
Non-volatile fatty acids, per cent. . . . .	92.85	62.53	62.91	55.76
Molecular weight of fatty acids . . . . .	278.1	270.2	273.3	269.1
Melting-point of fatty acids . . . . .	35-36°	45-46°	46°	51°

With regard to these results, the author points out that the fact that volatile acids are produced during the oxidation process is shown by the decrease in the *Hehner* and inner saponification values. The increase in the amount of unsaponifiable matter in B is only apparent, since B and B<sub>1</sub> are both fractions of the same oxidation products, and the greater proportion of unsaponifiable matter was removed by the preliminary treatment with petroleum spirit which gave B.

The general conclusion arrived at on this point is that during the oxidation of fats and oils the unsaponifiable matter remains intact, and new substances are not formed from it.

Unlike the oxy-fatty acids of liver oils (*Zeit. angew. Chem.*, 1891, 643), those of cottonseed oil are completely soluble in ether.

The foregoing method of analysis affords a means of examining the course of oxidation during the drying of linseed oil, and is also applicable to the examination of unoxidised fats and oils, as is seen in the following examples:—

	OX-TALLOW	OLIVE OIL	BUTTER-FAT
Saponification value	192.0	188.4	225.9
Inner saponification value	103.8	188.1	145.2
Hehner value	95.58	95.26	87.60
Unsapnifiable matter	0.11	0.98	0.24
Oxy-fatty acids	0.13	0.18	0.14
Non-volatile fatty acids	95.34	94.07	87.22
Molecular weight of fatty acids	275.0	280.1	264.7

From these results it is manifest that when, as in the case of tallow and olive oil, the total saponification and inner saponification values are nearly identical, the amount of volatile or of oxy-fatty acids must be insignificant. Butter-fat, on the other hand, by reason of its volatile acids, shows a considerable difference (40.7) between the two values, and the Reichert-Meissl value (36.3 for 5 grm.) can be calculated from this difference. This calculated value is higher than the normal, owing to the fact that the Reichert value only represents a portion of the total volatile acids.

Hehner and Mitchell (*Analyst*, Dec., 1898) have made a number of experiments confirming those of Hazura and others as to the oxidation and bromination products of linseed and other drying oils. As a result of these experiments the following method (given in substantially their own words) is proposed for examination of these oils:—

“When an oil, the fatty acids of which give insoluble bromo-compounds, is dissolved in ether or other suitable solvent, and bromine is added, there is an immediate precipitate produced, which can be washed readily and efficiently. The precipitate can be collected either in a Soxhlet tube, if the quantity taken is small, or on a counterpoised filter, but we recommend the method employed for the estimation of stearic acid in mixtures of fatty acids (see page 250); but instead of filtering through cotton, we find the best filtering material to be thin, flexible chamois leather tied over the end of the small thistle funnel, from which any adhering precipitate can afterward readily be removed by washing.

From 1 to 2 grm. of the sample are dissolved in 40 c.c. of ether, to which a few c.c. of glacial acetic acid are added, the precipitate forming being more granular from such a mixture than when ether alone is employed. The solution is cooled in an ice-chest and bromine added, the flask being preferably left all night in the ice. This, however, is not essential for ordinary working. The liquid is filtered off

by the suction funnel attached to a pump, the flask washed out with four successive portions of ether at  $0^{\circ}\text{C}$ ., and the residue dried in the flask to constant weight. Even when ether at ordinary temperatures is used, no considerable error is introduced.

Various samples of pure linseed oil were examined by this method, with the following results —

SAMPLE	OIL TAKEN	WEIGHT PRECIPITATA	PERCENTAGE OF DEPOSIT
A. . .	1 3226	0.3158	23.86
A. . .	3 1905	0.7573	24.42
B. . .	0.6792	0.1765	25.8
C. . .	1 0000	0.2439	24.8
C. . .	1 0000	0.2500	25.0

A sample of walnut oil gave, in two determinations, 1.9 and 1.42 per cent. of bromo compound. Poppy oil gave no deposit, nor did Brazil nut oil, maize oil, cottonseed oil, olive oil, Japanese wood oil, almond oil. Mixtures of linseed oil and other oils gave percentages of bromo-compound in proportion to the percentage of linseed oil, as will be seen from the following table:—

OILS USED	LINSEED OIL, PER CENT	INSOLUBLE BROMIDE, PER CENT	LINSEED OIL, CALCULATED FROM BROMIDE
Linseed A and Walnut . . .	69.0	16.6	69.0
" " " " " " " " " " " "	88.2	9.3	88.1
Linseed A and Maize Oil " " " " " " " " " " " "	52.0	12.4	50.8
" " " " " " " " " " " "	50.5	12.2	50.0
" " " " " " " " " " " "	51.7	12.6	51.6

It will be seen from the above figures that the determination of the amount of the precipitate can usefully serve for testing the purity of unoxidised linseed oil. More extended investigation as to the variation in the proportion of the precipitate yielding substance would, of course, be necessary, although as far as we have gone the variation appears to be small.

Considerable interest is attached to the nature and composition of the insoluble bromo compound. From its origin it cannot be identical with the acid hexabromide; this is also shown by its melting-point, which is from  $143.5^{\circ}$  to  $144^{\circ}\text{C}$ ., against hexabromide ( $177^{\circ}\text{C}$ ., Hazura,  $180^{\circ}\text{C}$ ., to  $181^{\circ}\text{C}$ ., *Hehner and Mitchell*). If it were the hexabromo-linolenic ester, it would contain 62.28 per cent of bromine. It cannot be linolic tetrabromo ester with 52.23 per cent. bromine, since maize oil does not furnish any insoluble compound, while the free acids readily yield large amounts of the acid bromo-derivative. We have made a considerable number of bromine determinations which gave remarkably constant results. In various preparations we

found 56.38, 55.7, 56.38, 56.32, 55.55, 56.17, and 56.32 per cent. bromine. This percentage is too low for the hexabromo-ester and too high for the tetrabromo-compound. Dr. Streathfield, of the Finsbury Technical College, was kind enough to make carbon and hydrogen determination of a specimen of the material. Its ultimate composition was as follows—

Carbon	32.97
Hydrogen	5.12
Bromine	56.18
Oxygen	4.44
Ash	0.99
	<hr/> 100.00

Calculated for the ash-free material, the composition is as follows:—

Carbon	33.29
Hydrogen	5.18
Bromine	56.74
Oxygen	4.40
	<hr/> 100.00

We are inclined to attribute to the bromo-compound the formula  $C_{57}H_{96}O_4Br_{14}$ , which would require—

Carbon	34.27
Hydrogen	4.81
Oxygen	4.81
Bromine	56.11
	<hr/> 100.00

On account of its insolubility, the substance could not be purified by crystallisation. In addition, the presence of mineral matter, probably derived from the oil itself, would tend to make deductions from the results still more uncertain. The percentage of bromine in the substance strongly points towards a mixed bromo-ester, and we suggest, very tentatively, the following formula:—



which, however, cannot be definitely accepted until a perfectly pure specimen has been examined. We are the more inclined towards a mixed formula, since the existence of such mixed esters has been fairly well proved in the case of butter-fat, and also because it is impossible to separate, even by recrystallisation persistently carried out, the stearin from palmitin contained in animal fats. When, on the other hand, the esters are broken up by saponification, the separation is

readily effected, and from the fatty acids separated from linseed oil a nearly pure hexabromide is readily obtained "

The following percentages of insoluble brominated compound were obtained from various oils —

Rape oil	0 0
Mustard-husk oil	1 5
Cod oil	42 9
Codliver oil	35 5
Shark oil	22 0
Whale oil	25 0

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The composition of a weighed residue consisting of sugar, glycerol, and neutral salts can be determined as follows, provided that both sugar and glycerol are present in reasonable proportion. Dissolve the residue in 9 times its weight of water—that is, use nine times as many c.c. of water to effect solution as there are grams of residue. Ascertain the specific gravity of this solution, and then evaporate it to dryness, ignite the residue gently, moisten with acetic acid to reconvert any carbonate into acetate, dry at 100°, and weigh. Then dissolve the residue in such a quantity of water as will produce a solution of the same measure as that evaporated. Ascertain the specific gravity of this solution, and subtract it from that of the solution of the original residue, when the difference will be that due to the glycerol and sugar present. As 10 per cent of glycerol increases the specific gravity of water by 24.0 (water = 1000), and 10 per cent. of sugar by 40.3, the proportion of each present in 100 parts of the residue may be found by the following equations, in which *g* is the percentage of glycerol, *s* that of sugar, *a* that of neutralised ash, and *d* the difference between the specific gravity of the 10 per cent. solution of the original residue and that of the solution of ash made up to the same volume —

$$g = \frac{40.3 - 40.3a - d}{163}, \text{ and } s = 100 - (a - g).$$

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O Foister (*Chem Zeit*, 1898, 421) has devised an apparatus for extraction with immiscible solvents, the construction of which is shown in fig. 14. The cylinder *A* should hold about 1 liter. Two openings are not necessary, since both tubes may pass through the same cork, but the arrangement shown is more convenient. 600 cc of the soap solution as free as possible from alcohol are placed in the cylinder, 300 cc. of ether added and the mixture

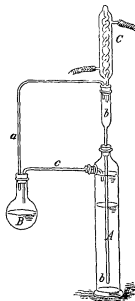


FIG 14

well shaken. The rest of the apparatus is then attached. The flask *B* has a capacity of 200 to 300 cc.; the ether in it is heated by a water-bath. The vapor passes by *a* into *b*, the condensed liquid flows to the bottom of *A* and rises through the soap solution, the upper layer of ether returns through *c* into *B*. The tube *c* should not extend into the liquid in *B*. A small quantity of aqueous liquid may collect at intervals in *B* and should be removed. The ethereal solution will require four or five washings with water, to remove dissolved soap. It is stated that the apparatus will remove all but traces of cholesterol from a stearin soap by four hours' extraction

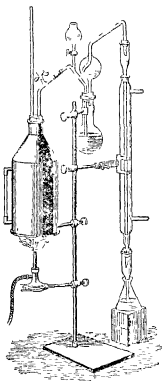


FIG 15 —KJELDAHL APPARATUS  
(See next page)

H. Bremer (*Zeitschr f. Unter. d. Nahr u. Genuss*) has described a new apparatus for the determination of nitrogen by the Kjeldahl method (fig 15). The same flask is used for the digestion in hot sulphuric acid as for the distillation, thus obviating the necessity of transferring from one to another. The flask is of about 250 c c. capacity and has a long neck 35 mm wide. The digestion in this flask is said to occupy scarcely any longer time than in the flask usually employed for the purpose. As soon as the digestion is completed, the flask is cooled and attached to the rest of the apparatus as shown in the figure. The soda solution is introduced through the funnel and the distillation carried by means of a current of steam. The apparatus can also be used for the determination of ammonia by distillation with magnesia or barium carbonate.



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